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Trace Organics Variation Across the Wastewater Treatment System of a Class-B Refinery and Estimate of Removal of Refractory Organics by Add-On Mixed-Media Filtration and Granular Activated Carbon at Pilot Scale

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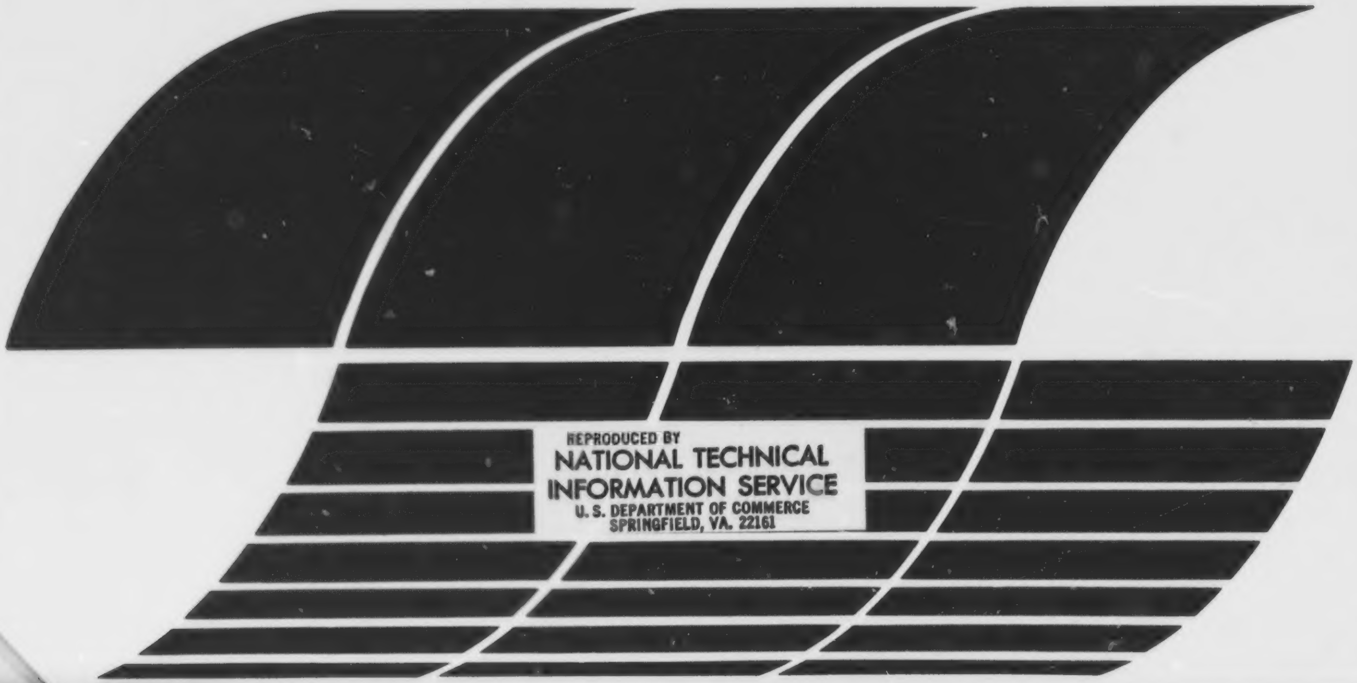
Trace Organics Variation Across the Wastewater Treatment System of a Class-B Refinery

Interagency Energy/Environment R&D Program Report



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Estimate of Removal of Refractory Organics by Add-On Mixed-Media Filtration and Granular Activated Carbon at Pilot Scale

by

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ABSTRACT

Wastewater at SOHIO's Toledo refinery was sampled every four hours for four successive days in December, 1976. Effluents from the full-scale system (dissolved-air-flotation [DAF] unit and final clarifier for the activated-sludge unit) and an add-on pilot-scale unit (mixed-media filter and activated-carbon columns) were sampled for analysis of common wastewater parameters and trace organic compounds. Grab samples taken every four hours were composited daily. Organics were isolated into acid, base, and neutral fractions. Four-day composites of these daily extracts were analyzed by capillary-column gas chromatography/mass spectrometry. Some 304 compounds were identified in the neutral fraction of the DAF effluent and removal of these organics by the activated-sludge and add-on treatment units was estimated. Numerous data for the approximate concentration of organic compounds are presented. Common wastewater parameters are also presented for comparison to specific organics concentration data.

The activated-sludge unit removed aromatic compounds better than it did nonaromatics whereas the activated-carbon unit was better at removal of nonaromatic compounds. Average percentage removal of those organics present in the DAF effluent was: >99% (activated sludge), ~0% (mixed-media filter), and <1% (activated carbon). Of the ~1% of trace organics remaining in the final-clarifier effluent, 81% (by weight) were removed by the activated carbon. Because of variations in extraction efficiencies, amount of sample injected, losses on the GC column and transfer lines, and other sources of error, these are only approximate removal estimates.

EXECUTIVE SUMMARY

This report presents the results of research conducted by Argonne National Laboratory jointly for the U.S. EPA's Robert S. Kerr Environmental Research Laboratory and for the U.S. DOE's Division of Environmental Control Technology, Office of Assistant Secretary for Environment. The primary aim of the research was to evaluate the efficiency of pilot-scale granular activated carbon for the removal of organic compounds refractory to the activated-sludge treatment system of a Class B petroleum refinery that met BPT ("best practicable technology") in 1977. In order to achieve this goal, it was necessary to characterize the trace organic compounds present not only in the effluent from an add-on mixed-media/activated-carbon pilot-scale unit, but also those compounds in the effluents from two of the wastewater treatment steps (the dissolved-air-flotation and activated-sludge treatment steps) that preceded the pilot-scale unit. The research approach that was adopted and the major results are as follows.

a) Add-on pilot-scale setup at Class-B refinery

Argonne assisted the Robert S. Kerr Environmental Research Laboratory (RSKERL) in setting up its mobile, pilot-scale equipment at SOHIO's Toledo refinery, a 120,000 BPSD refinery having crude topping, catalytic cracking, and coking. The RSKERL pilot-scale equipment consisted of two 6-in.-ID glass, up-flow carbon columns, with a total bed depth of 6 ft, preceded by one 6-in.-ID, mixed-media filter. A constant flow rate of 0.25 gpm was maintained and a carbon analyzer was used to confirm that TOC breakthrough (carbon-column overloading with organics) did not occur.

b) Wastewater sampling and organics extractions

Grab samples of wastewater taken every 4 hr were composited every 24 hr at each of the four sampling points mentioned earlier (the effluents from the dissolved-air-flotation, final-clarifier, mixed-media-filtration, and activated-carbon units). Each day's composite samples were iced and air shipped to RSKERL for extraction. This procedure was followed for four consecutive days. Organic compounds were isolated by a liquid-liquid extraction technique using methylene chloride followed by extract concentration and ampuling for shipment. RSKERL supplied Argonne with 1-mL solutions of the acid, base, and neutral fractions composited over the 24-hr sampling periods.

c) Identification of wastewater organic compounds

The 12 fractions of the composited extractions were analyzed by gas chromatography/mass spectrometry (GC/MS), using capillary columns of the wall-coated variety and Grob-type splitless injection. Comprehensive identification of organics in the effluent from the dissolved air flotation (DAF) unit was undertaken. Over 300 compounds were identified in the neutral fraction using (primarily) single-ion chromatograms. The concentrations of the organics in the final clarifier (FC), mixed-media filtration (MMF), and activated-carbon (AC) effluents were so low that a special procedure had to be instituted for their identification. It was necessary to assume that each organic compound identified in the DAF effluent was present also in the FC, MMF, and AC effluents, but at much lower concentrations. This assumption was equivalent to using the extract of the DAF effluent as a "standard mixture." Identification of each organic in the FC, MMF, and AC extracts was based on retention time, presence of major ions, and semi-quantification of the area or peak height of each major ion.

d) Results (neutral-fraction organics)

Predominant types of compounds in the neutral fraction of the DAF effluent were n-alkanes, toluene, C_2, C_3 and C_4 benzenes, naphthalene, methyl naphthalenes and C_2-naphthalenes, phenanthrene, anthracene, and methyl phenanthrenes and anthracenes, present in concentrations of about 10-700 ppb (expressed as concentration in the wastewater, and not corrected for extraction efficiency).

There was extensive removal of trace organics by the activated sludge unit, no measurable removal by the add-on mixed-media filter unit, and varying removal, where measurable, of the remaining (refractory) organics by the add-on activated-carbon unit. With regard to the n-alkanes, C_9 through C_{31}, the percent removal by activated sludge was greatest for C_{10} and fell off gradually as carbon number increased. With activated carbon, there was again a gradual decrease in percent removal as carbon number increased, due probably to less adsorption ability for higher alkanes.

Percent removals of branched alkanes by the activated sludge and by the activated carbon, where measurable, are in the same range as the n-alkanes.

Cycloalkanes (or alkenes) were removed by the activated-sludge unit in much the same way as the n-alkanes but none could be detected in the activated-carbon effluent, probably because of their extremely low concentrations in the final-clarifier effluent.

Alkylated benzenes were drastically removed by the activated sludge; additional removal by activated carbon appeared to be limited. Indan and tetralin-type molecules exhibited similar behavior.

Naphthalene and alkylated naphthalenes were substantially removed by activated sludge and only partially removed by activated carbon.

Alkylated benzothiophenes, dibenzothiophenes, PNAs, and alkylated PNAs were present in very small quantities and removal percentages were difficult to estimate.

In general, the activated-sludge unit removed aromatic compounds better than nonaromatic compounds whereas activated carbon showed greatest removal efficiency on nonaromatic compounds of the neutral fraction.

e) Results (acid-fraction organics)

Over 30 phenols were found in the acid fraction of the DAF effluent, ranging in concentration from 1 to 50 ppb. Predominant phenols were phenol, the cresols, an unidentified xylenol, and 2,3-xylenol. The activated-sludge unit was very effective in removing phenols. Three alkylated phenols were removed at levels of >99.9%. A measure of the efficiency of the activated-carbon unit for removal of phenols was not possible due to the extremely low concentrations (or absence) of phenols in the effluent from the final clarifier.

f) Results (base-fraction organics)

More than 70 compounds were found in the base fraction of the DAF effluent. Some of these were not organic bases, reflecting incomplete separations in the extraction process. Very small amounts of alkylated pyridines were present, such as picolines, ethyl pyridines, lutidines, ethyl picolines, collidines and ethyl lutidines. Small amounts of alkylated quinolines, C_1, C_2, and C_3s, and appreciable quantities of aniline and alkylated anilines were present. Although analysis of the data showed that the activated-sludge unit did remove base-fraction organics, little can be said owing to the very small concentrations involved.

g) Results (common wastewater parameters)

Also reported herein are the results of a parallel effort at wastewater characterization that was conducted by SOHIO's Warrensville Research Center. Common wastewater parameters were run daily on composites of 4-hr grab samples collected in parallel with those taken for trace organics characterization. Average performance data for the 4-day study showed either no effect or only a minor effect of the mixed-media filter, but a major effect of activated-carbon unit, on final-clarifier effluent. The activated-carbon effluent was of a quality equal to or better than the plant intake water (from Maumee Bay) for all seven parameters measured. The final clarifier effluent was slightly higher in concentration with regard to cyanide, COD, BOD, and TOC and equal or better with regard to O + G and suspended solids than the intake water and activated carbon effluent. However, since only very low levels (ppb range) of organics were found by GC-MS analysis of the final clarifier effluent, the organics contributing to the BOD, COD, and TOC concentrations are compounds not amenable to extraction and/or GC-MS analysis and probably consist of high molecular weight compounds such as humic acids and natural by-products of bacterial action.

h) Removal of trace organics by granular activated carbon (GAC) at pilot scale

A limitation of this study is that data were obtained from the pilot-scale GAC unit for only four days on *fresh* carbon. These data permit inferences about refractory organics removal only when a GAC adsorber is started up. It was not possible to speculate on 1) compound breakthrough characteristics with respect to percent GAC bed saturation as a function of TOC or COD adsorbing capacity or 2) when regeneration is necessary.

1 INTRODUCTION

1.1 BACKGROUND

At the time this study was initiated, the 1983 BATEA model for wastewater treatment for the petroleum refining industry, as proposed by the Environmental Protection Agency (EPA), consisted of the following treatment sequence: biological treatment, mixed-media filtration, or its equivalent, and granular activated carbon. Thus, the proposed 1983 model consisted of fixed-bed activated-carbon adsorption added onto the 1977 "best-practicable-technology" (BPT) which consisted of biological treatment followed by final polishing. (The U.S. Court of Appeals Ruling of August 11, 1976, however, remanded for reconsideration by the EPA Administrator the 1983 guidelines for petroleum refining including the requirement for granular activated carbon in the treatment sequence.)

An important step in evaluating the efficacy of the BATEA model involves documentation of the ability of fixed-bed activated carbon to remove trace organic compounds that are refractory to the biological plus mixed-media treatment steps. This study was carried out to try to determine the relative organic compositions of the effluents from the biological, mixed-media (polishing), and granular-activated-carbon treatment steps. An effort was made to characterize the trace organic compounds in these effluents at a Class B refinery having treatment meeting BPT limitations. The results would serve primarily as guidance for determining the need for a larger-scale study and would not necessarily be used to predict the performance of a full-scale system.

1.2 STUDY OBJECTIVES AND SCOPE

The objectives of this study were

a) characterization of trace organic compounds across the full-scale wastewater treatment system at a Class B petroleum refinery that met BPT,

b) characterization of trace organics in effluents from add-on filtration and carbon adsorption at pilot scale, and

c) estimation of the ability to remove trace organics by the full scale and the add-on pilot-scale units.

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The scope of the study involved taking water samples every four hours for four days at the following points (Fig. 1.1):

1) the refinery's raw-water intake main,
2) the effluent stream from the dissolved-air-flotation (DAF) unit,
3) the effluent stream from the final clarifier (FC),
4) the pilot mixed-media filter (MMF) effluent stream, and
5) the pilot activated-carbon (AC)-column effluent stream.

The four-hour grab samples were to be composited daily. Trace organics from the composited samples were to be extracted as acid, base, and neutral fractions for characterization by capillary-column gas chromatography/mass spectrometry (GC/MS).

Comparisons of the trace organic compositions of the effluents listed above were undertaken by

a) attempting a comprehensive identification of the organics in the DAF effluent,
b) determining the retention time and the major ions associated with each organic compound in the DAF effluent,
c) measuring the peak height (or area) of the major ions of each organic in the DAF effluent,
d) measuring, in the FC, MMF, and AC effluents, the peak height (or area) of the previously-determined major ions of each organic, and

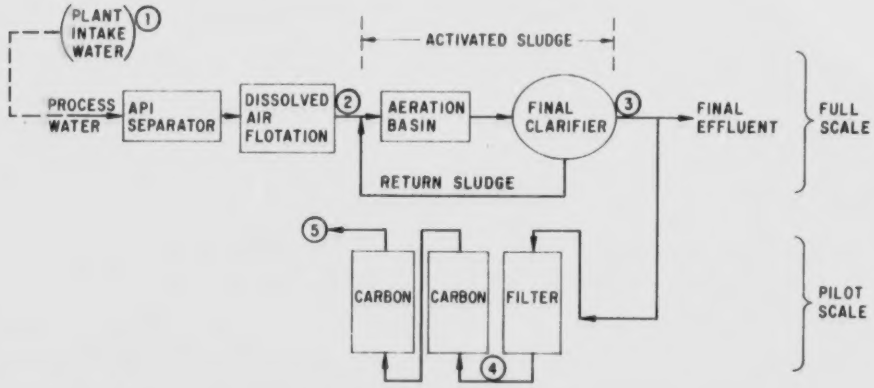
PLANT INTAKE WATER
①
ACTIVATED SLUDGE
PROCESS WATER
API SEPARATOR
DISSOLVED AIR FLOTATION
②
AERATION BASIN
FINAL CLARIFIER
③
FINAL EFFLUENT
FULL SCALE
RETURN SLUDGE
⑤
CARBON
CARBON
FILTER
④
PILOT SCALE

Fig. 1.1. Schematic Diagram Showing Proposed Sampling Points at the Plant Intake(1) and in the Full-Scale(2,3) and Pilot-Scale(4,5) Wastewater Treatment Systems of a Class-B Refinery

e) calculating the percent reduction of peak height (or area) of each major ion in going from the DAF to the FC, MMF, and AC effluents.

The above assumes that extraction efficiencies are equivalent (not necessarily 100%) for each organic compound in the DAF, FC, MMF, and AC effluents.

1.3 PREVIOUS WORK

Burlingame (1977) characterized the organic compounds in three grab samples of wastewater from an unspecified Class-B refinery. The wastewater samples were taken subsequent to the API separator, subsequent to the Pasveer oxidation ditch and clarifier, and subsequent to the non-aerated lagoons. Burlingame used capillary-column GC and high-resolution MS to identify and inventory the major compound types in the neutral fraction of the three samples. Pfeffer, Harrison, and Raphaelian (1977) reported on the preliminary results of the present work, for SOHIO's Class B refinery at Toledo, Ohio.

With the exception of these two preliminary studies, we are unaware of any published works that attempt to characterize all of the measurable trace organics across a full-scale refinery wastewater treatment system. Nor have we found any material in the literature regarding the removal efficiencies of activated carbon for trace or refractory organics in biologically treated refinery wastewater.

Matthews (1978) has prepared a comprehensive review of the treatment of selected industrial wastewaters, including petroleum refinery wastewater, with activated carbon. No studies such as the present were uncovered in Matthews' search of the literature.

1.4 REFINERY SELECTION

Considerable time was allocated to refinery selection, as there was sufficient funding to study only one refinery. Repeated discussions and meetings were held with members of the API's W-20 Task Group to arrive at a "representative" refinery; however, all agreed that a truly representative refinery did not exist. It was agreed to acquire permission from a Class B refinery whose final effluent quality met BPT. Other selection criteria included intake water quality and variability, refinery turnaround plans, final-effluent quality, raw-waste loading, and hydraulic detention times typifying the activated sludge process at a Class B refinery.

Agreement was reached in September 1976 to conduct the study at SOHIO's Toledo refinery. This is a Class B refinery (crude topping and catalytic cracking) with coking, having a crude capacity of 120,000 BPSD. The treatment train at that time consisted of an API Separator, a dissolved-air-flotation (DAF) unit, an extended aeration type activated sludge unit, and a final clarifier. The final effluent quality routinely satisfied BPT requirements with the exception of suspended solids. Following a 1-month turnaround period, the wastewater treatment system returned to steady state in November 1976, one month before sampling for this study began.

2 EXPERIMENTAL PROCEDURES

2.1 PILOT-SCALE EQUIPMENT

2.1.1 Setup

EPA's Robert S. Kerr Environmental Research Laboratory (RSKERL) furnished a mobile laboratory trailer that was positioned near the final clarifier. Facilities aboard the trailer included 6-in.-ID glass columns for filtration and carbon adsorption (Fig. 2.1), a TOC analyzer for monitoring organic carbon breakthrough, pumping and distribution capability, and sampling gear. The sampling equipment, pumps, and distribution lines were fabricated and so installed that the only materials in contact with water moving through the pilot treatment system were stainless steel, glass, Teflon, and polypropylene. A stainless-steel reservoir was used for backwashing (Fig. 2.2). Pumps had polyethylene impellers and housings. Sampling points 2 and 3 (Fig. 2.2) were removable steel plugs. A 25-ft inlet line connected the clarifier weir trough to the primary pump. Sampling points aboard the trailer were: 1) SOHIO's final clarifier effluent, 2) pilot mixed-media filter effluent, and 3) pilot carbon-column effluent (Fig. 2.2).

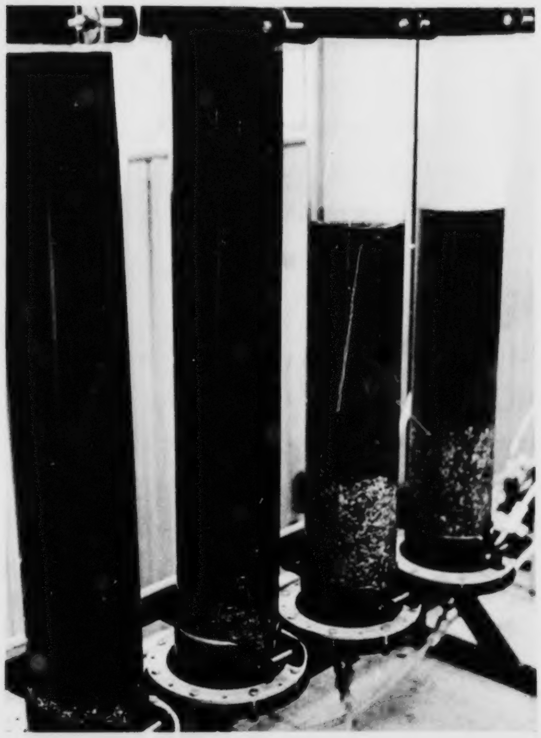

Fig. 2.1. Pilot-Scale Activated-Carbon Columns and Mixed-Media Filters

Two, parallel, down-flow mixed-media filters (Fig. 2.1) were used. While one was operating for 24 hr, the second, having been backwashed, was ready for use the next day. Figure 2.2 shows the configuration of the filtering bed: anthrafilt, washed ungraded sand, and washed gravel. Sand used had an Effective Size of 0.2 mm and a Uniformity Coefficient of 4.5.

Backwashing was accomplished by alternately pulsing with air and pumping carbon-column effluent.

Two up-flow carbon columns (Fig. 2.1) were packed as shown in Fig. 2.2 and operated in series to achieve a total bed depth of 6 feet. A constant flow rate of 0.25 gpm was maintained. The reactivated carbon used was Calgon's Adsorption Service Carbon. Calgon's analysis of a sample from the lot used at Toledo gave these results:

Apparent Density[a] (g/cc):	0.51
Molasses Number:[b]	282
Iodine Number:[c]	821
Sieve Result (mesh)	8x40

Column packing was accomplished by trickling material into each water-filled glass column.

2.1.2 Operation

Following packing, the filters were cleaned by back flushing with plant tap water for about one hour. Each filter was backwashed prior to usage by pulsing with air, to kick up the anthrafilt and the top few inches of sand, and then backwashing with final-clarifier effluent to sweep out the dislodged suspended solids. This operation was performed for about one hour. During the run, backwashing was performed in a similar manner using carbon effluent; then the column was allowed to stand for about 23 hours while full of the carbon-column effluent.

On the day prior to the study, the system was operated for about one hour on final-clarifier effluent and then shut down until the study. Flow control was accomplished by mechanical constriction (Fig. 2.2) on the carbon-column discharge line. This eliminated H_2S bubbles released in the carbon

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[a] Weight per unit volume of homogeneous activated carbon.

[b] Calculated from the ratio of optical densities of the filtrate of a molasses solution treated with standard activated carbon and the test activated carbon. This is the test method of Pittsburgh Activated Carbon Co. Molasses number is assumed to reflect transitional-pore surface area.

[c] The milligrams of iodine adsorbed by one gram of carbon at an equilibrium filtrate concentration of 0.02N iodine. It is measured by contacting a single sample of carbon with an iodine solution and extrapolating to 0.02N via an assumed isotherm slope. Iodine number can be correlated with ability to adsorb low-molecular-weight substances and is assumed to reflect small-pore surface area.

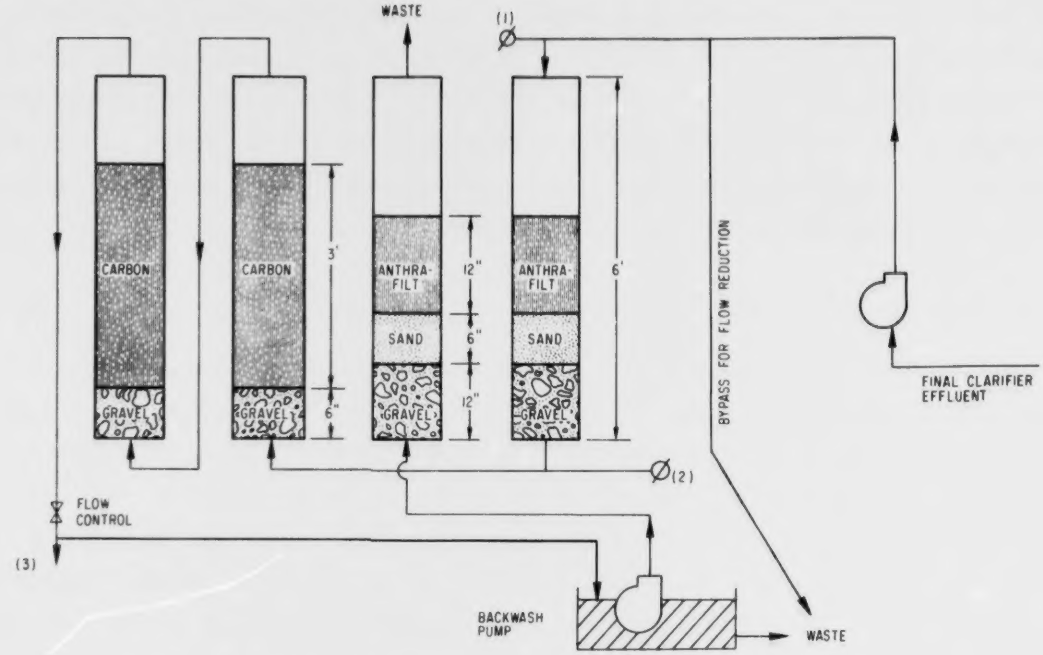

WASTE
(1)
CARBON
CARBON
ANTHRA-FILT
ANTHRA-FILT
SAND
SAND
GRAVEL
GRAVEL
GRAVEL
GRAVEL
3'
6"
12"
6"
12"
6'
BYPASS FOR FLOW REDUCTION
FINAL CLARIFIER EFFLUENT
(2)
FLOW CONTROL
(3)
BACKWASH PUMP
WASTE

Fig. 2.2. Schematic of Add-On Treatment System and Sampling Points for Effluent from Final-Clarifier(1), Mixed-Media Filter Unit(2), and Carbon-Column Unit(3)

columns when flow control was attempted at the discharge side of the pump feeding final clarifier effluent to the filter.

The add-on treatment system was operated at 1/4 gpm, resulting in about 36 min contact time for the carbon at a surface loading rate of 1.27 gpm/ft^2. The residence time (36 min) is the empty-bed residence time, V/Q. No biological growth was noted on the carbon during the study.

Flow to the columns was initiated at 4:00 A.M. on the first day of the study. Following the 8:00 A.M. sampling each day, the system was shut down. The filters were reversed; the backwashed filter was switched to the filtration mode, and the previously used filter was plumbed for backwash. The columns were started again, and the flow adjusted. Total shut-down time was about 15 min.

During the study, there were no significant recorded changes in flow through the plant wastewater treatment system, as measured by the biofeed pumping rates (that is, the wastewater influent to the aeration basin). Note that, waste sludge being insignificant, the final-clarifier effluent and biofeed flows were assumed to be equal. Aeration time was of the order of 16-18 hours and mixed-liquor volatile suspended solids concentration in the aeration basin was 4440 mg/L, during the study. These values are noted here because the performance and operating conditions of the activated sludge unit can have a significant effect on the organics removal capabilities of granular activated-carbon columns (Kim, et al., 1976).

2.2 WASTEWATER SAMPLING

Samples of wastewater (~420 mL each) were taken and iced every four hours (8A, 12N, 4P, 8P, 12M, and 4A) at each of the five locations given in Sections 1.2 and 2.1. Plant intake water was sampled at a wet well on the negative side of the pump that lifts water to the process units. The well receives water by gravity flow from Maumee Bay, Lake Erie. Effluent from the dissolved air flotation (DAF) unit was sampled from a valve on the discharge pump that lifts DAF effluent to the aeration basin. This valve remained open during the 4-day study.

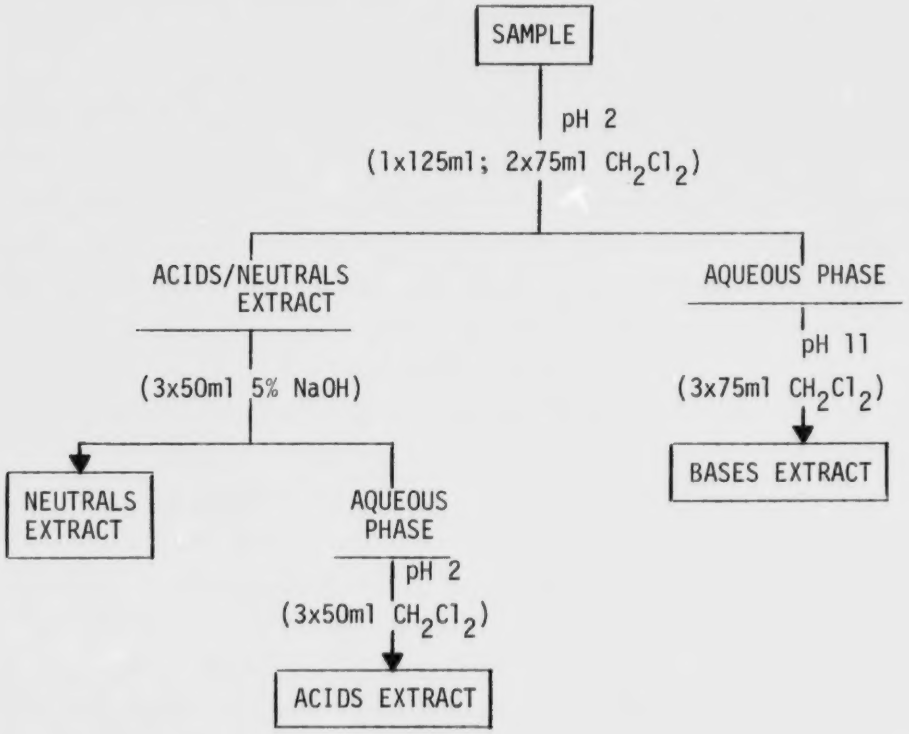
Every 24 hr a composite sample (~2.5 L) was made up, from the previous day's 4-hr individual samples, for each of the five sampling points. Each daily set of composited samples was transported in ice chests to Detroit for air shipment to Ada, Oklahoma. The samples arrived at RSKERL in Ada within 9 hr of final compositing in Toledo.

Attention was given to decontaminating material coming in contact with water samples. All glassware was cleaned by firing, maintaining 550°C for 1 hour. Sample-bottle caps contained Teflon liners which had been cleaned by Soxlet extraction with methylene chloride, the solvent later used in the laboratory for extracting the organics from the water samples.

Two problems occurred which should be noted. The 12N grab was missed during the first 24-hr compositing period owing to a power failure. Secondly, the validity of the composite sample of carbon-column effluent for the first day and for 1/6 of the second day is somewhat doubtful owing to an error in sampling. The flow being only 1/4 gpm and the total volume of sample required for SOHIO and Argonne analyses being over 2 gallons, the flow restriction was removed during sampling. The flow was probably 1 gpm at this time. However, soluble total organic carbon values recorded before and after this point showed no appreciable differences. Total organic carbon values were measured to assure that no break-through occurred during the study. (Samples were taken of the final-clarifier, mixed-media, and carbon-column effluents (usually at 8:00 A.M. and 12:00 N) for determination of soluble total organic carbon.)

2.3 ISOLATION OF ORGANICS

Personnel at EPA's RSKERL prepared the composited water samples for GC/MS analysis by Argonne. This involved the following tedious liquid-liquid extraction sequence using methylene chloride.


SAMPLE
pH 2
(1x125ml; 2x75ml CH_2Cl_2)
ACIDS/NEUTRALS EXTRACT
AQUEOUS PHASE
(3x50ml 5% NaOH)
pH 11
(3x75ml CH_2Cl_2)
BASES EXTRACT
NEUTRALS EXTRACT
AQUEOUS PHASE
pH 2
(3x50ml CH_2Cl_2)
ACIDS EXTRACT

Again, all glassware was fired for organics decontamination. A major problem was emulsion formation, requiring emulsion breaking and phase separation by various techniques. Each organic extract was dried by passing through anhydrous sodium sulfate and the solvent was stripped, resulting in 1 mL of concentrated extract which was sealed in a glass ampul. A period of 9 man-hours was involved in preparing each sample to the ampul stage; there were 20 samples requiring this preparation.

Of the 24-hr-composited 3780-mL water samples from each of the sampling points, 2500 mL were extracted to give 200 mL each of neutral, acid, and base fractions. Of the 200-mL extract of each fraction, 125 mL were concentrated to 1 mL extracts (one for each of 4 days, 3 fractions, and 5 sampling points - a total of sixty 1-mL extracts). For use in GC/MS analysis, 0.2 mL of each of four 1-mL extracts (one for each day) were combined to give a 4-day composite extract which was evaporated in a 1-mL, cone-shaped vial to 50 μL.

2.4 GC/MS ANALYTICAL PROCEDURES

2.4.1 General Description of the GC/MS System

Analysis of the specific organics in the extracts was performed on a Hewlett-Packard 5982A GC/MS equipped with a Hewlett-Packard 5933A Data System consisting of a 2100S Computer with 16K, 16-bit-word core memory, 7900A Dual Disc Drive with 2.5M bytes/disc memory, 5948A A/D Converter, 6131C D/A Converter, and a Tektronix 4012 Display Terminal. A 5930 HP GC was used in place of the 5700 Series HP GC normally delivered with the 5982A GC/MS. Peripheral equipment included a Tektronix 4631 Hard Copy Unit and a Zeta 130-10 Incremental Plotter. Discs with the Aldermaston AWRE Spectral Library, the HP Contributed Libraries, and the EPA/NIH Spectral Library were also available along with an Anderson Jacobson AD 342 Acoustic Coupler for connecting to the Cyphernetics Mass Spectral Search System in Ann Arbor, Michigan. During the course of the study, it was found that the time required for analysis and workup of data far exceeded that required for collection of data. This was due partly to the great complexity of the samples and partly to the high resolution of peaks by the capillary columns used. Thus, a time sharing data system, the HP 5934A, was obtained; it consisted of a 21MX Computer with 32K, 16 bit word core memory, 7900A Dual Disc Drive with 2.5M bytes/disc memory, 5948B Data Subsystem (A/D and D/A Converters), and a Tektronix 4012 Display Terminal. With this data system, data could be collected during GC/MS runs while previously collected data could be analyzed. Also, the 5933A Data System could be used for analyzing previously collected data.

2.4.2 Capillary-Column GC/MS

Due to the anticipated complexity of samples that were to be analyzed, it was felt that capillary columns of the wall-coated variety should be used to afford the greatest resolution possible. Although support-coated open tubular (SCOT) type columns are simpler to use, the wall-coated open tubular (WCOT) columns were used because of their greater resolution, less susceptibility to tailing due to adsorptive effects, and their ability to pass higher-boiling components such as PNAs, which were of interest in this study. With WCOT columns, leak-proof and low-dead-volume connections are required to avoid tailing of peaks and care was taken to ensure that this was the case. A modified split/splitless Hewlett-Packard Grob-type injection system was used for the capillary columns. The end of the column was connected to glass-lined stainless-steel tubing with an ID of 0.5 mm. The glass-lined stainless-steel tubing was connected directly to a line going to the mass spectrometer source. Since no separator, such as a jet or membrane separator, was used, all components of a mixture exiting the column entered the mass spectrometer. Therefore, there could not be discrimination in the amount of each component reaching the mass spectrometer as there is with separators. Assuming the individual components are not lost in the injection system, the column, or the glass-lined stainless-steel-tubing transfer line, the amount of each component in the mixture reaching the source of the mass spectrometer is a true representation of the quantity injected on column.

The glass-lined stainless-steel-tubing transfer line was wrapped carefully with insulated nichrome wire, insulated with glass wool and glass electrical tape. With this method of heating, the transfer line could be left at lower temperatures due to the more uniform heating and compounds passing through the transfer line were less likely to decompose due to hot spots typically found in commercial instruments where other devices are used for heating the transfer line. As a result, gains in sensitivity, particularly of the higher boiling components, are noticeable.

Since the sample extracts consisted of small amounts of organics in a solvent, it was found necessary to use Grob-type splitless injection. As opposed to split operation, the Grob system avoids the loss of large amounts of the sample and the discrimination of components of the mixture. Also, peaks tend to be sharper due to the so-called "solvent" effect whereby the plug formed at the beginning of the column is smaller because the solvent acts as a barrier to diffusion of the plug and tends to concentrate the plug. Moreover, in splitless operation, the septum is continuously purged during the run thereby avoiding components of the septum to enter the column. However, it was found that, between runs, septum-bleed would enter the column, deteriorating the resolution of the column during runs. Thus, a modification of the system was made whereby the injection port was automatically put into the purged state between runs or overnight.

Aside from the well-known increased resolution of capillary columns over packed columns, there are other aspects of capillary column GC/MS that make the use of capillary columns desirable. First, since in mass spectrometry, the mass spectrum, or abundance of each ion, is recorded at a specific instant, there is no integrating effect. Thus, even if one can see a total-ion chromatographic peak, one does not necessarily get an interpretable mass spectrum. With capillary column GC/MS, because of the narrowness of the peak, the actual amount of compound reaching the source per unit time is considerably higher than with packed columns and, therefore, sensitivity is increased and possible interpretation is enhanced. Second, capillary columns have drastically reduced column bleed as compared to packed columns. Although present data systems are equipped with methods for subtracting background, this procedure never works very well, particularly with trace amounts of organics. From the outset, it is better to have as little background as possible. Third, all the compound exiting the capillary column enters the mass spectrometer, whereas with packed columns, only part (typically less than 50%) gets through the separator to the mass spectrometer source. There are certain high-boiling compounds that never get through packed columns due either to adsorptive effects or to decomposition. On the other hand, capillary columns pass the same high-boiling compounds at considerably lower temperatures.

2.4.3 Specific Problems Encountered in the Analysis of Extracts

In initial capillary column GC/MS studies of the neutral fraction of the DAF, FC, MMF, and AC samples, it was found that, whereas there were appreciable amounts of organics in the DAF samples, the concentration of organics in the FC, MMF, and AC was well below the detection limit by typical GC/MS procedures, except for a very few organics. For example, a major component in the DAF is n-pentadecane; it was present at a concentration of approximately 240 ng on column (that is, when injected onto the column at 100 times dilution). It was reduced by the activated sludge to approximately 90 ng on column and, by the activated carbon, to approximately 8.1 ng on column. The majority of organics in the DAF have a lower concentration than that of n-pentadecane. Since the lower limit of detection under ideal conditions by typical GC/MS procedures is approximately 10 ng on column, it would appear that a study of the reduction of the organics in the DAF effluent by the activated-sludge and activated-carbon units might be impossible with the possible exception of a very few compounds. Even with single-ion techniques (mass fragmentography), the detection of most of the organics would at best be difficult in the FC and AC effluents. Also, due to the large number of different organics (over 300) in the DAF, the use of single-ion techniques would be cumbersome; present-day data systems for GC/MS are set up for monitoring only a limited number of ions and are, therefore, adaptable to looking at only a few compounds during a run. Based on these observations, it appeared that the identification of organics in the FC and AC samples would be impossible.

Because of the foregoing problems an assumption had to be made; namely, those organics that are present in the DAF effluent are present also in the FC and AC effluent, but at much lower concentrations. Under such an assumption, one can examine the FC- and AC-effluent GC/MS data for those specific organics present in the DAF effluent. This method is equivalent to using the extract of the DAF effluent as a "standard mixture," and requires a comprehensive identification of the organics in the DAF-effluent extract and documentation of the mass spectrum, major ions, and retention time of each component. The identification of the organics in the FC and AC effluents is, therefore, based on retention time and the presence of major ions and the semi-quantification on the area or peak height of the major ions. (Of course, in identifying a component in the FC and measuring its concentration, one can not differentiate between whether the component had arisen from incomplete removal by the activated sludge or from bacterial decomposition of another component.) Although the method is simple in principle, it is difficult to carry out because most of the more than 300 components in the DAF effluent are present in only minute quantities and, in many cases, there is an overlap of peaks even with the use of high resolution capillary columns. (An exhaustive analysis by massgrams indicates that there are probably 400-600 components in the DAF effluent and many of the components overlap in high resolution capillary column GC/MS.)

However, with the use of capillary columns, the identification of small quantities of organics is enhanced since the background due to column bleed is low and background due to other compounds is often absent because of the high resolving power of capillary columns. Also, the probability of overlapping peaks having the same major ions is low, and there are, in practice, relatively few instances in which interferences take place.

2.4.4 Techniques for Identifying Organics in the Extracts

It was found that the major components in the DAF effluent were benzene, toluene, all isomers of C_2, C_3 and C_4-benzenes, naphthalene, alkylated naphthalenes, alkanes and alkenes. There were also many indans, anthracenes, phenanthrenes and fluorenes. It would appear that standards would be of use in identifying what is present in the DAF effluent. However, it was found that the commercially available standards are only those simpler compounds that are easily identifiable by GC/MS such as n-alkanes and alkylated benzenes up to C_3 or C_4-benzenes and a few indans, naphthalenes, anthracenes, phenanthrenes, and branched alkanes. One is familiar with the great number of isomers possible with alkanes up to C_{25} but listings of aromatic compounds are less frequently available. A very limited listing of such aromatics, along with the number actually found in the neutral fraction of the DAF effluent, is found in Table 2.1.

The retention times of isomers of hydrocarbons occur in groups when chromatographed on a non-polar column, since separation takes place predominantly according to the boiling point of each compound. A representation of this effect is shown in Fig. 2.3, which is taken from data of a GC/MS run of the DAF-effluent neutral fraction on a 50-m OV-101 column programmed from 20°C to 240°C at 2°C/minute with 2-min hold at 20°C.

The identification of the type of isomer within a group is relatively easy since the fragmentation pattern of isomers is fairly predictable. For example, take the C_3-benzene isomers; Table 2.2 is a listing of approximate abundances of key ions useful for differentiating between these isomers. If one assumes a tendency to reach the stable tropylium ion (from $C_6H_5CH_2^+$) and that the loss of an alkyl group is preferred to the loss of hydrogen, one can explain the patterns that arise with these C_3-benzenes. For example, to reach a tropylium ion from an ethyl toluene, either a methyl or hydrogen ion could

Table 2.1. Number of Possible Isomers of Alkylated Benzenes and Some PNAs Commonly Found in the Neutral DAF Fraction

	Possible Isomers	Found in DAF
Benzene	1	1
Toluene	1	1
C_2-Benzenes	4	4
C_3-Benzenes	8	8
C_4-Benzenes	22	19
C_5-Benzenes	50	19
C_6-Benzenes	135	16
Indan	1	1
C_1-Indans	7	2
C_2-Indans	29	4
Tetralin	1	1
C_1-Tetralins	4	1
C_2-Tetralins	16	2
Naphthalene	1	1
C_1-Naphthalenes	2	2
C_2-Naphthalenes	12	7
Phenanthrene/anthracene	2	2
C_1-Phenanthrenes/Anthracenes	8	5
C_2-Phenanthrenes/Anthracenes	51	9
Fluorene	1	1
C_1-Fluorenes	7	3
C_2-Fluorenes	29	7
Benzothiophene	1	1
C_1-Benzothiophenes	6	4
C_2-Benzothiophenes	21	7
Dibenzothiophene	1	1
C_1-Dibenzothiophenes	7	2
C_2-Dibenzothiophenes	28	1

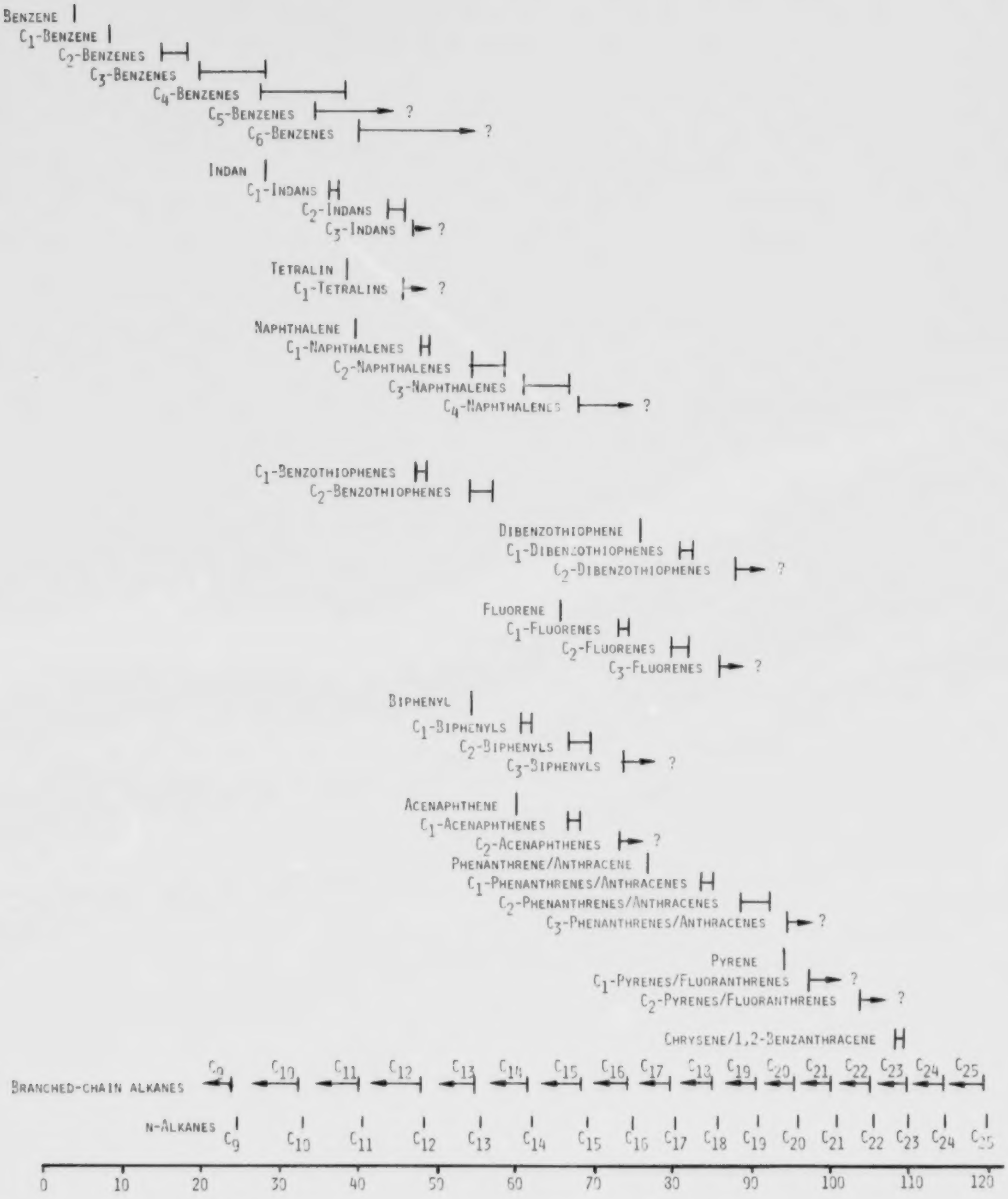


Fig. 2.3. Groupings of Major Classes of Compounds Present in the Neutral DAF Fraction as a Function of Retention Time, Chromatographed on a 50-m OV-101 Capillary Column Programmed at 2°C/Min from 20-240°C with 2-Min Hold at 20°C

Table 2.2. Abundances of Key Ions of C_3-Benzenes

Compounds	Ions 91	105	119	120
1,2,3-Trimethyl benzene	5	100	10	45
1,2,4-Trimethyl benzene	5	100	10	50
1,3,5-Trimethyl benzene	5	100	10	60
o-Ethyl toluene	5	100	Trace	25
m-Ethyl toluene	5	100	Trace	25
p-Ethyl toluene	5	100	Trace	25
n-Propyl benzene	100	85	None	45
i-Propyl benzene	5	100	None	25

be lost but methyl loss is preferred and only a trace of the 119 ion is formed. With i-propylbenzene, the loss of a methyl group is further enhanced with the formation of a relatively stable secondary carbonium ion, and thus there is no perceptible 119 ion. With n-propyl benzene, the loss of ethyl leads to the tropylium ion with a mass of 91. Finally, with the trimethyl benzenes, there are appreciable amounts of 119 formed due to the loss of a hydrogen. These patterns (Table 2.2) can be seen nicely in the 91, 105, 119, and 120 massgram plots of the DAF in Fig. 2.4. The trimethyl benzenes (numbers 16, 18, and 25) have appreciable amounts of the 119 ion. The n-propyl benzene (number 13) has an appreciable 91 ion. The ethyl toluenes (numbers 14, 15, and 17) have predominantly the 105 ion and traces of the 119 ion. Finally, i-propyl benzene (number 13) has a 105 ion but no 119 ion.

Also, as shown in Fig. 2.5, it can be seen that the retention time is related to the boiling point of the C_3-benzenes.

It can be shown that similar identifications, based on the fragmentation pattern and boiling point, can be made for other alkyl-substituted benzenes and alkyl-substituted naphthalenes, anthracenes, phenanthrenes, etc., provided a non-polar liquid phase is used for the GC column. [As the alkyl-substituted aromatic becomes more fully alkylated (such as C_5, C_6, etc.), correlations with boiling point break down because the molecules are more alkane-like and, therefore, similar to the liquid phase and partitioning with or solubility in the liquid phase is greater.]

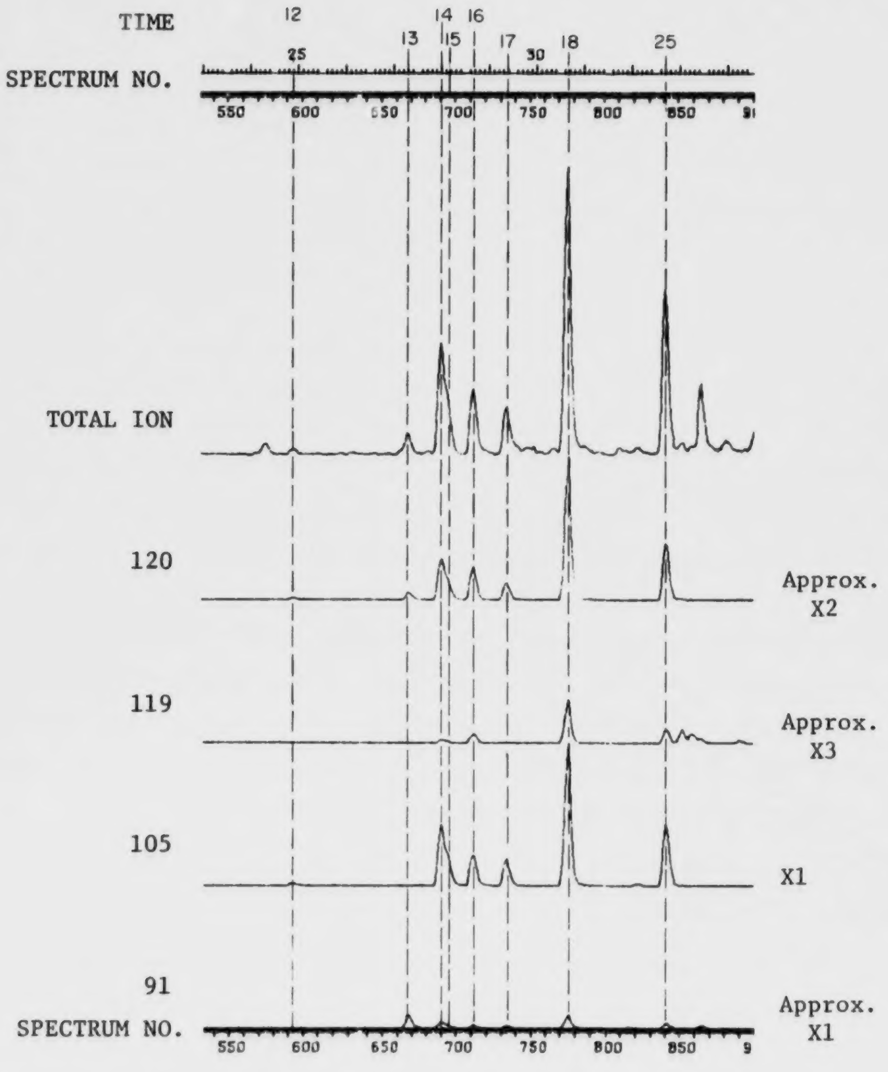


Fig. 2.4. Massgram Plots of Key Ions (91, 105, 119, and 120) of C_3-Benzenes used in Identifying the Specific Isomers

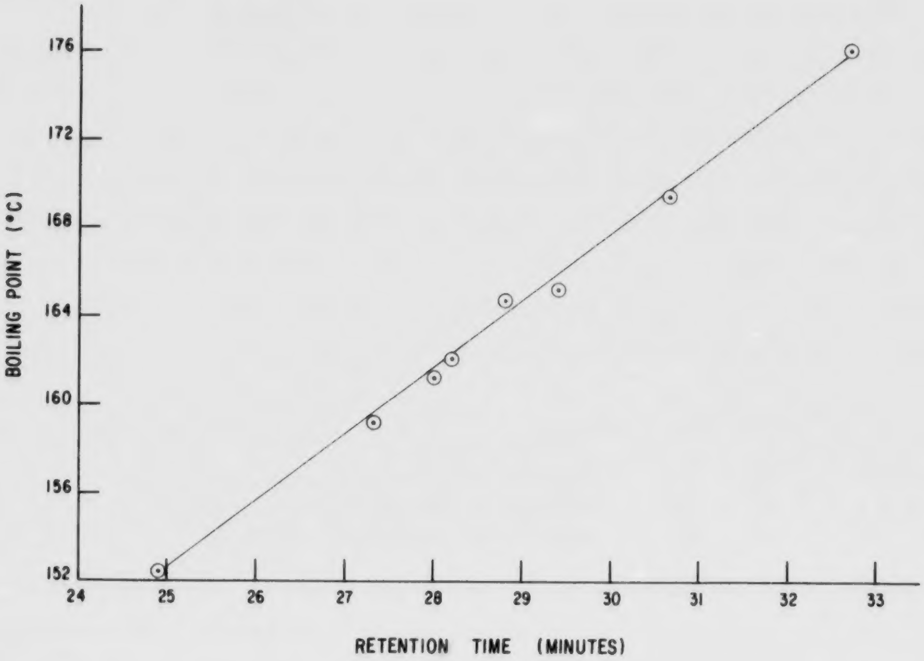


Fig. 2.5. Retention Time Versus Boiling Point of C_3-Benzenes

The major components of the neutral fraction of the DAF were identified by their mass spectra and the amount present was determined by measuring the peak area of the peak in the total-ion chromatogram and comparing it to the peak area of a standard from the same class of compounds. (Of course, it should be noted that generally GC/MS is not suitable for truly quantitative measurements and data generated must be considered only semi-quantitative. Also, percent recoveries with liquid-liquid extraction, stability, etc. are difficult parameters to determine, particularly with such complex mixtures as the neutral fraction of the DAF effluent.)

Whereas the amount of a major component in the neutral fraction of the DAF effluent was derived from the peak area of its peak in the total-ion chromatogram, the determination of the amount of the same compound in the FC and AC effluents was measured by determining the peak area of its major ion because, with the extremely low concentration of these compounds in the FC and AC effluents, major ions are more selective and impurities can be "filtered out."

In addition to identifying the major components in the neutral fraction of the DAF effluent by their mass spectra, an exhaustive massgram analysis of minor components was undertaken. It was found that most of the compounds in the DAF effluent were alkylated benzenes, naphthalenes, anthracenes, phenanthrenes, chrysenes, pyrenes, fluorenes, acenaphthenes, biphenyls, acenaphylenes, benzothiophenes, dibenzothiophenes, indans, and tetralins. There were also n-alkanes, branched alkanes and some cycloalkanes (or alkenes). Identification of alcohols was, at best, difficult because of their lack of molecular ion. It was found convenient to do a plot of four ions at a time:

Ion	Identification
M^+	molecular ion
$M^+ - 1$	molecular ion minus one hydrogen
$M^+ - 15$	molecular ion minus one methyl
$M^+ - 29$	molecular ion minus one ethyl

Most alkylated aromatics gave peaks of at least two of these ions and, in general, identification of the compound was not difficult. To make certain that the massgram peaks associated with a compound were, in fact, from the same compound, a line could be drawn through massgram peaks with relatively high accuracy since the Zeta plotter is accurate to one-hundred of an inch. If the peaks were coincident in retention time, it was assumed that those ions were from the same compound (see Fig. 2.4 for an example of this). Ions used for massgram plots are shown in Table 2.3.

In conclusion, the identification of organics in the neutral fraction of the FC and MMF/AC effluents by typical GC/MS procedures is difficult at best, since most of the compounds are present at concentrations approaching the limit of detection. However, by doing a comprehensive study, identifying each organic in the DAF efffluent and determining the retention times of the major ions associated with each organic in the DAF-effluent extract, it was found that organics in the DAF effluent also could be identified in the FC and MFF/AC effluents.

2.4.5 Column Effects and Semi-Quantitative Analysis of the Extracts

Whereas the analysis by capillary-column GC/MS of components in a mixture, with concentrations of each component ranging from 50-150 ng on column, is relatively simple, problems were encountered with the extracts because the range of concentrations was from well below 1 ng to 300 ng on column. It is

Table 2.3. Ions Used for Massgram Plots

Ions				Compound Type
Group 1				
91	105	119	120	C_3-benzenes
105	119	133	134	C_4-benzenes, benzothiophene
119	133	147	148	C_5-benzenes, C_1-benzothiophenes
133	147	161	162	C_6-benzenes, C_2-benzothiophenes
Group 2				
117	118	131	132	indan, C_1-indans, tetralin
117	131	145	146	C_2-indans, C_1-tetralins
131	145	159	160	C_3-indans, C_2-tetralins
Group 3				
127	128	141	142	naphthalene, C_1-naphthalenes
127	141	155	156	C_2-naphthalenes
141	155	169	170	C_3-naphthalenes
155	169	183	184	C_4-naphthalenes, dibenzothiophene
169	183	197	198	C_5-naphthalenes, C_1-dibenzothiophenes
Group 4				
153	154	167	168	biphenyl, acenaphthene, C_1-biphenyls, C_1-acenaphthenes
153	167	181	182	C_2-biphenyls, C_2-acenaphthenes
167	181	195	196	C_3-biphenyls, C_3-acenaphthenes
Group 5				
151	152	165	166	acenaphthylene, C_1-acenaphthylenes, fluorene
151	165	179	180	C_2-acenaphthylenes, C_1-fluorenes
165	179	193	194	C_3-acenaphthylenes, C_2-fluorenes
179	193	207	208	C_4-acenaphthylenes, C_3-fluorenes
Group 6				
177	178	191	192	phenanthrene/anthracene, C_1-phenanthrenes/anthracenes
177	191	205	206	C_2-phenanthrenes/anthracenes
191	205	219	220	C_3-phenanthrenes/anthracenes
Group 7				
201	202	215	216	pyrene,[a] C_1-pyrenes
201	215	229	230	C_2-pyrenes
Group 8				
227	228	241	242	chrysene,[b] C_1-chrysenes
227	241	255	256	C_2-chrysenes
Group 9				
57	99	83	97	alkanes, alkenes

[a] Also includes fluoranthenes, aceanthrylenes, acephenanthylenes

[b] Also includes tetracenes, triphenylenes, tetraphenes

well known, in packed-column GC, that the peak height (or area) does not fall off linearly with the concentration, but that, as the concentration becomes low, the peak height (or area) falls off precipitiously. When no peak is observed with the injection of a small amount of compound, we say that the compound was lost in the column. Actually, what is really happening is that the compound is tied up by adsorption sites in the liquid phase or support and elutes gradually from the column, possibly with a long tail. It is, therefore, lost in the baseline. (Actually, the same phenomenon occurs with larger quantities of compound injected on the column, but the effect is not noticeable because the perecentage loss is small.) With capillary columns, adsorption can be a severe problem, since the glass surface is quite large relative to the amount of compound passing through the column. Thus, at low concentrations, measurements of concentration tend to be too low.

Additionally, a second problem can arise with capillary columns. Since the liquid phase is small per unit volume, band spreading can occur when a compound saturates the liquid phase and codissolves additional compound. Typically, an overloaded capillary-column GC peak rises slowly, reaches a maximum and quickly goes back to baseline much like a sawtooth wave. Thus, at higher concentrations, concentration can not be accurately measured by peak height. On the other hand, normally, area measurements are not affected. However, there are saturation effects that take place in a GC/MS system. Table 2.4 shows an example of this. The on-column concentration of the 100-fold diluted DAF-effluent sample of 2-methyl naphthalene is approximately 170 ng based on a 60 ng standard. This turns out to be approximately 380

Table 2.4. Area Counts of 50-Fold and 100-Fold Diluted Samples for Some Compounds in the DAF Effluent

Compound	Ion	DAF 50-Fold Dilution	DAF 100-Fold Dilution	Ratio of Area Counts
2-Methyl naphthalene	142	82889	64351	1.29
Naphthalene	128	68867	56201	1.23
1-Methyl naphthalene	142	50633	37639	1.35
p,m-Xylenes	91	45806	29896	1.53
o-Xylene	91	27903	17283	1.61
Ethyl benzene	91	12637	7516	1.68

counts per nanogram. It would be expected that the area counts would double in each case for the 50-fold versus the 100-fold dilution. However, as can be seen in Table 2.4, the ratio is low for high counts and increases for lower counts. Thus, at high concentrations the measurements of concentration tends to be low.

With the measurement of concentration being too low, at both high concentration due to overload and low concentration due to adsorption on the column, it would seem desirable to make corrections for these effects. However, since the DAF, FC, MMF, and AC effluent samples contain so many compounds, such an approach would be cumbersome. Also, it would seem feasible to dilute the sample to measure the strong peaks and concentrate the sample to measure the weak peaks. However, this introduces a new set of variables. In any case, considerable effort would be expended in doing standards at various concentrations and looking for interactions.

There are many techniques used for making capillary columns and these varied techniques lead to columns that are different in their resolution and adsorption. In this study, three capillary columns were used: a Perkin-Elmer 50-m OV-101, a Perkin-Elmer 50-m OV-17, and a LKB 20-m SE-30. The intention was to use the non-polar 50-m OV-101 for the neutral fractions, the 50-m OV-17 for the acid and base fractions, and the 20-m SE-30 for the higher boiling neutral compounds such as the PNAs.

2.4.6 Sources of Error in Determination of the Absolute Amount of Organics in the DAF, FC, and AC Extracts and the Percent Removal of Organics by Activated Sludge and the Add-On Treatment System

It is well known that measurement of the specific amount of each component in a mixture by GC/MS is at best semi-quantitative; however, this study required some idea of the effectiveness of full and pilot-scale treatment systems in removing trace organics from the wastewater stream. In determining organics removal from GC/MS data there are several potential sources of error; a few will be cited here. First, there is the problem of extraction efficiency. It would be expected that, in those samples with high concentrations of organics, such as the DAF effluent, extraction efficiency would be relatively high ("like dissolves like"). Thus, in samples with low concentrations of organics, such as the AC effluent, extraction efficiency would be relatively low. Moreover, the extraction efficiency would vary from compound to compound depending upon the solvent used, the concentration of the component to be extracted, and the polarity of the component. Second, the amount of sample injected, in this case 3 μL, can vary from sample to sample. This variation is usually in the range of ± 3% for a 3 μL injection. Third, in splitless operation, a small portion of the sample, usually less than 1%, is lost during purge. A more difficult parameter to measure, in this regard, is whether any discrimination has taken place in this loss. Fourth, in preparing the DAF extract, it was necessary to dilute the sample 100-fold relative to the FC and AC extracts. Fifth, as mentioned previously, the measurement of concentration tends to be low at both high concentrations (due to overload) and at low concentrations (due to adsorption on the column). As a result, at very low concentrations, there is often no measurable signal, although a compound may have been injected onto the column. Sixth, there is a peculiarity in the mass spectrometer and data system that leads to inaccuracies. The data system makes a comparison of the shape of a peak of an ion with a theoretical quadrupole peak shape (non-Gaussian). If that peak is similar and above a certain threshold in area (to reject noise), parameters set by the user, the peak is accepted. Since a typical peak in a quadrupole or, for that matter, in a magnetic-sector instrument, is truly a mixture of pulses of ions concentrated around the centroid of the peak, noise, and other types of pulses can destroy the shape of the peak and, thereby, the peak is rejected. An example of this can be seen in Table 3.9 (Section 3) in the 142 ion column under "Activated Carbon Effluent" where one sees unexpected zeros in the data: 12, 27, 56, 69, 50, 0, 24, 9, etc. These occurrences lead to inaccuracies in the measurement of the area of such a peak. They occur most often with weak and/or high mass peaks.

Taking into consideration all these sources of error, it would appear difficult to obtain an accurate or absolute measurement of the amount of each component in the extracts and, indeed, this is the case. However, within any one sample or injection, it is possible to make comparisons of the amounts of the various components. Also, it is possible to make comparisons of percent removal by activated sludge (or the add-on treatment system) for different components within a mixture since it would be expected that the errors introduced are generally the same for all components within said mixture. That is, although the actual values for percent reduction of each compound in a mixture might be quite inaccurate, comparisons of percent removal of compounds within a group and also of groups of compounds can be made. For example, whereas the reported percent removal of n-alkanes and alkyl benzenes might be inaccurate in an absolute sense, the relative removal of n-alkanes might be reasonably precise. Likewise, whereas the reported percent removal of each member of a series of n-alkanes might be inaccurate in an absolute sense, the relative differences in percent removal could be reasonably precise. To carry out these comparisons and to uncover trends, it was found necessary to report more significant figures than is warranted considering the potential sources of error. For example, a percent reduction of n-decane of 99.98% does not mean that it is accurate to four significant figures or even three significant figures. However, it is useful to use such a number for comparison with other n-alkanes such as n-octadecane (99.54%) and n-pentacosane (99.36%) showing a trend of reducing percent removal as the carbon number increases. Likewise, it is useful for comparison with branched alkanes which range from 99.73% to 99.96%, as described in the next section.

2.5 DETERMINATION OF ANCILLARY PARAMETERS

Personnel from the SOHIO Research Center, Warrensville, Ohio, collected samples for determination of standard wastewater parameters at the same times and locations as were sampled by Argonne and RSKERL personnel for the trace organics study. The SOHIO samples were iced and transported by car from Toledo to Warrensville each morning. All analyses were started within 5 hr after the daily composited samples left Toledo.

The following standard wastewater parameters were determined according to U.S. EPA-recommended procedures (U.S. EPA, 1974): oil and grease, cyanide, phenol, chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total suspended solids (TSS). Total organic carbon (TOC) was determined according to an ASTM procedure (American Society for Testing and Materials).

3 RESULTS

3.1 NEUTRAL-FRACTION ORGANIC COMPOUNDS

Appendix A lists 304 compounds identified in the neutral fraction of the DAF effluent. Only a very few of these compounds could be identified directly by their mass spectra. However, with the use of massgrams, the majority of compounds were identified. (In certain cases, the exact isomer was not determined.) Appendix D presents massgram plots and tentative identifications of organics found in a GC/MS run with a 50-m OV-101 column programmed from 20° to 240°C at 2°C/min, whose total-ion chromatogram is shown in Fig. 3.1. Appendix E presents mass spectra for various compounds in the neutral fraction of the DAF effluent, listed according to increasing retention time.

It can be seen (Appendix A) that the predominant types of compounds in the neutral fraction of the DAF effluent were n-alkanes, toluene, C_2, C_3 and C_4-benzenes, naphthalene, methyl naphthalenes and C_2-naphthalenes, phenanthrene, anthracene, and methyl phenanthrenes and anthracenes. These compounds were present in the DAF effluent at concentrations from approximately 10 ppb to 700 ppb.

Generally, there was substantial removal of organics by the activated sludge unit, no measurable removal by the add-on mixed-media filter unit, and varying removal, where measurable, of many organics by the add-on activated carbon unit. (For purposes of this study, it will be assumed that all of the removal of organics by the entire add-on pilot-scale unit was due to the activated carbon. Therefore, all results referred to as percent removals by activated carbon represent, in fact, organics removal by the entire add-on treatment system.)

Tables 3.1-3.7 list the major organics found in the neutral fraction of the DAF effluent. In Table 3.1, which is a listing of the n-alkanes, C_9 through C_{31}, it can be seen that there is very significant removal of organics by the activated sludge (in the range of 99.33%-99.98% removal) and a substantial additional removal of organics by the activated carbon (in the range of 70.2%-97.9%). It is interesting to note that percent removal is greatest for C_{10} and falls off gradually as the carbon number increases. It appears that either the bacteria are more efficient in degrading lower alkanes or there is

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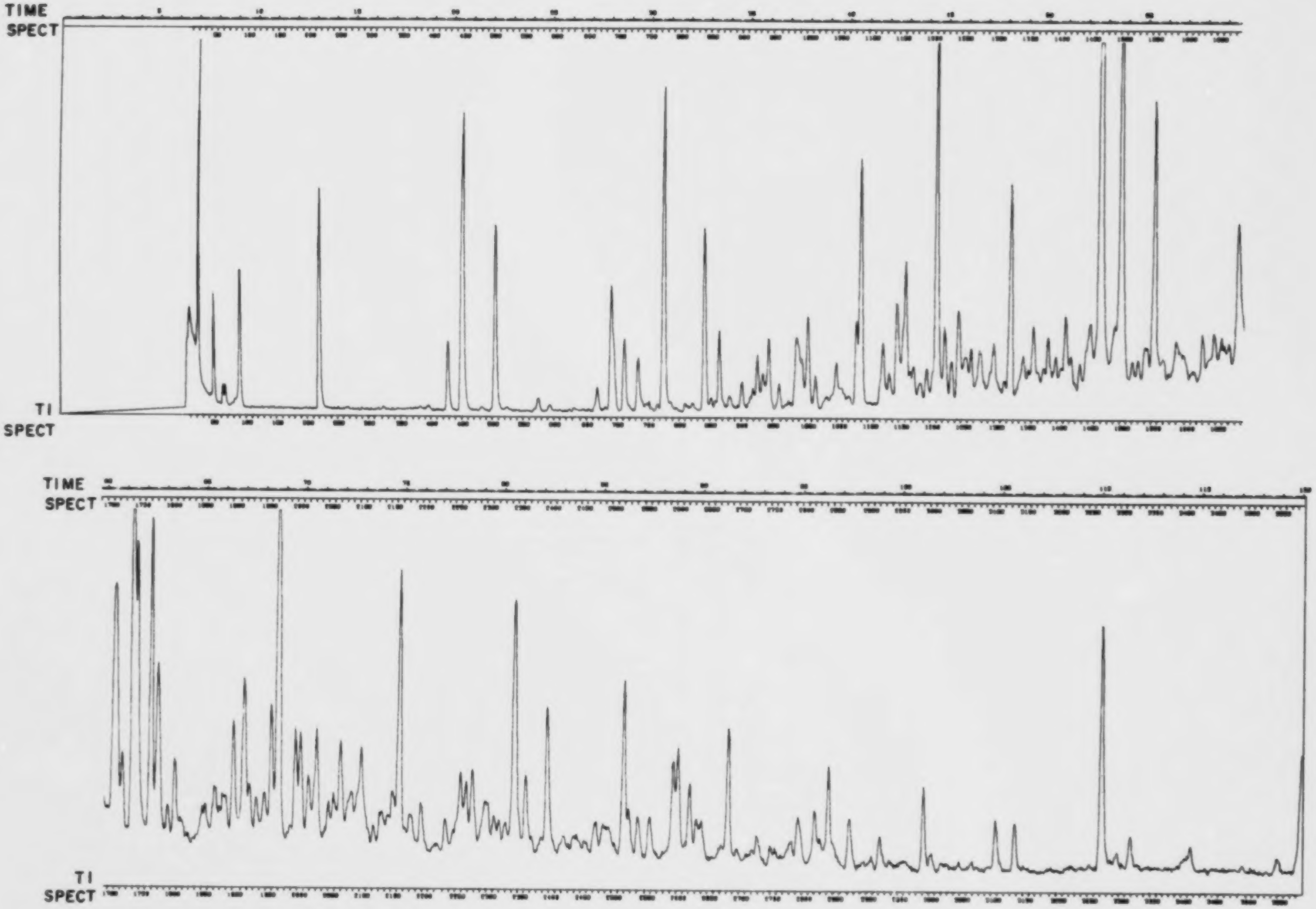

Fig. 3.1. Total-Ion Chromatogram of Neutral Fraction of DAF Effluent (Diluted 100-Fold) Made Using a 50-m OV-101 Column Programmed from 20-240°C with a 2-min Hold at 20°C.

wastage in sludge, or, possibly, there is considerable loss into the air of the lower alkanes due to their greater volatility. With the activated carbon, here again, there is a gradual decline in the percent removal as the carbon number increases. Apparently, the higher n-alkanes are less readily adsorbed onto the activated carbon. Possibly, as the size of the molecule increases, the molecule can not get into the pores of the activated carbon surface and is, therefore, less readily adsorbed.

In Table 3.2, branched alkanes are listed. Percent removals of these alkanes by the activated sludge and by the activated carbon, where measurable, are in the same range as the n-alkanes.

Cycloalkanes (or alkenes) are removed by the activated sludge in much the same way as the n-alkanes but none can be detected in the activated carbon effluent, possibly because of the low concentrations in the final-clarifier effluent.

The removal of alkylated benzenes (Table 3.3) by the activated sludge is drastic and ranges from 99.87-99.99%. Additional removal by activated carbon appears limited, ranging from 51.4-84.1%; however, data are scarce due to the low concentrations being measured. With indan and tetralin-type molecules, similar behavior is found (Table 3.4).

There is substantial reduction (99.69-99.99%) of naphthalene and alkylated naphthalenes by the activated sludge and varying reduction (37.7-91.7%) by the activated carbon (Table 3.5).

With alkylated benzothiophenes and dibenzothiophenes (Table 3.6), which were present in small quantities, the percent removal by the activated sludge was in the range of 99.81-99.93% and the percent removal by activated carbon was in the range of 71.4-82.9%.

With PNAs and alkylated PNAs (Table 3.7), the picture is not clear, since generally these compounds were present in very small quantities. Measurable removal figures for the activated sludge were in the 99.65-99.99% range and PNAs were not detectable in the activated-carbon effluent with the exception of phenanthrene and anthracene which were reduced 52.8% by the activated carbon.

The results in Tables 3.1-3.7 are summarized in Table 3.8. It can be seen by inspection of Table 3.8 that the percent removal by the activated

Table 3.1. Concentration of n-Alkanes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
n-nonane	32	12	NM	ND
n-decane	128	48	99.98	ND
n-undecane	349	131	99.97	T
n-dodecane	544	204	99.83	97.9
n-tridecane	675	253	99.74	95.9
n-tetradecane	683	256	99.63	93.7
n-pentadecane	651	244	99.61	91.3
n-hexadecane	493	185	99.59	90.9
n-heptadecane	355	133	99.55	87.6
n-octadecane	261	98	99.54	86.9
n-nonadecane	205	77	99.55	88.4
n-eicosane	160	60	99.55	85.3
n-heneicosane	107	40	99.60	79.4
n-docosane[c]	64	24	99.40	80.3
n-tricosane[c]	61	23	99.55	82.6
n-tetracosane[c]	43	16	99.41	79.5
n-pentacosane[c]	32	12	99.36	70.2
n-hexacosane[c]	27	10	99.33	77.9
n-heptacosane[c]	19	7	99.43	T
n-octacosane[c]	13	5	99.36	T
n-nonacosane[c]	11	4	NM	T
n-triacotane[c]	NM	NM	T	T
n-heneitriacotane[c]	NM	NM	T	T

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final-clarifier effluent.

[c] 20-m SE-30 column.

T	Trace
NM	Not measurable due to interferences
ND	Not detectable

Table 3.2. Concentration of Cycloalkanes and Alkanes Other than n-Alkanes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound (number)	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Alkanes				
C_{13}-Alkane (97)	159	60	99.92	T
C_{13}-Alkane (117)	77	29	99.94	ND
C_{14}-Alkane (151)	196	74	99.80	T
C_{14}-Alkane (169)	246	92	99.96	78.7
Pristane	157	59	99.73	78.1
Phytane	67	25	99.94	58.8
Cycloalkanes[c]				
(19)	30	11	99.96	ND
(21)	21	8	99.94	ND
(44)	57	21	NM	ND
(45)	31	12	99.76	ND
(49)	41	15	99.98	ND
(83)	29	11	99.88	ND
(86)	27	10	99.86	ND
(127)	71	27	99.93	ND
(129)	42	16	99.95	ND
(176)	43	16	99.83	ND

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final-clarifier effluent.

[c] Also includes alkenes.

T	Trace
ND	Not detectable
NM	Not measurable due to interferences

Table 3.3. Concentration of Alkylated Benzenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Toluene	101	38	99.87	84.1
Ethyl benzene	35	13	99.95	66.7
p and m-Xylenes	187	70	99.97	76.6
o-Xylene	101	38	99.97	77.3
i-Propyl benzene	5	2	ND	ND
n-Propyl benzene	13	5	99.94	T
m-Ethyl toluene	93	35	99.98	71.2
o-Ethyl toluene	32	12	99.98	T
1,3,5-Trimethyl benzene	43	16	99.97	ND
1,2,4-Trimethyl benzene	176	66	99.98	44.9
1,2,3-Trimethyl benzene	96	36	99.98	60.0
n-Butyl benzene	8	3	T	ND
m-n-Propyl toluene	19	7	99.97	ND
o-n-Propyl toluene	13	5	99.96	ND
m-Diethyl benzene	13	5	T	ND
1,3-Dimethyl-5-ethyl benzene	29	11	99.98	ND
1,3-Dimethyl-4-ethyl benzene	37	14	99.98	ND
1,2-Dimethyl-4-ethyl benzene	43	16	99.99	ND
1,3-Dimethyl-2-ethyl benzene	16	6	ND	ND
1,2-Dimethyl-3-ethyl benzene	13	5	T	ND
1,2,4,5-Tetramethyl benzene	27	10	99.98	ND
1,2,3,5-Tetramethyl benzene	48	18	99.98	T
1,2,3,4-Tetramethyl benzene	64	24	99.99	51.4

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

T	Trace
ND	Not detectable

Table 3.4. Concentration of Indan and Tetralin and Related Compounds and Their Alkylated Derivatives in the Neutral Fraction of the Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound (number)	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Indan	93	35	99.98	50.0
1-methyl indan	104	39	99.98	T
2-methyl indan	61	23	99.99	ND
Ethyl indan	27	10	T	ND
Dimethyl indan (100)	61	23	99.98	T
Dimethyl indan (106)	11	4	ND	ND
Dimethyl indan (111)	35	13	99.97	ND
Trimethyl indan (118)	35	13	T	ND
Tetralin	11	4	ND	ND
Methyl tetralin (104)	64	24	T	ND
Ethyl tetralin (126)	27	10	99.93	ND
Dimethyl tetralin (131)	21	8	T	ND
Ethyl styrene (39)	19	7	ND	ND
Ethyl styrene (41)	48	18	99.98	ND
C_3-Styrene (71)	19	7	T	ND
C_3-Styrene (72)	72	27	99.99	ND
C_3-Styrene (74)	21	8	99.97	ND
C_3-Styrene (77)	53	20	99.99	ND

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

T Trace
ND Not detectable

Table 3.5. Concentration of Naphthalene and Alkylated Naphthalenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound (number)	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Naphthalene	197	74	99.99	37.7
1-Methyl naphthalene	448	168	99.99	44.9
2-Methyl naphthalene	259	97	99.99	33.3
Ethyl naphthalene (146)	77	29	99.98	55.8
Dimethyl naphthalene (149)	192	72	99.99	38.3
Dimethyl naphthalene (153)	NM	NM	--	--
Dimethyl naphthalene (154)	267	100	99.99	26.8
Dimethyl naphthalene (155)	203	76	99.99	I
Dimethyl naphthalene (158)	96	36	99.99	12.0
Dimethyl naphthalene (160)	45	17	99.94	37.5
C_3-Naphthalene (166)	24	9	99.74	T
C_3-Naphthalene (168)	21	8	99.69	87.7
C_3-Naphthalene (172)	160	60	99.91	91.7
C_3-Naphthalene (173)	45	17	99.76	T
C_3-Naphthalene (174)	37	14	99.90	T
C_3-Naphthalene (175)	51	19	99.95	
C_3-Naphthalene (177)	99	37	99.97	69.8
C_3-Naphthalene (178)	125	47	99.96	61.2
C_3-Naphthalene (180)	85	32	99.97	45.2
C_3-Naphthalene (181)	80	30	99.97	T
C_3-Naphthalene (183)	93	35	99.97	T

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

NM	Not measurable due to interferences
T	Trace
I	Increase in concentration

Table 3.6. Concentration of Alkylated Benzothiophenes and Dibenzothiophenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound (number)	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Methyl benzothiophene (109)	21	8	T	ND
Methyl benzothiophene (114)	16	6	99.91	71.4
Methyl benzothiophene (119)	13	5	99.87	ND
Methyl benzothiophene (121)	32	12	99.92	82.9
Ethyl benzothiophene (156)	11	4	99.85	ND
Dimethyl benzothiophene (143)	11	4	99.93	ND
Dimethyl benzothiophene (148)	16	6	99.91	ND
Dimethyl benzothiophene (150)	8	3	99.81	ND
Dimethyl benzothiophene (152)	8	3	99.83	ND
Dibenzothiophene	13	5	T(N)	ND

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of final clarifier effluent.

T	Trace
N	Noisy, possibly due to column bleed
ND	Not detectable

Table 3.7. PNAs and Alkylated PNAs Other than Naphthalenes in the Neutral Fraction of the DAF Effluent and Percent Removal by the Activated-Sludge and Activated-Carbon Units (50-m OV-101 Column, 3 μL Injection)

Compound (number)	Concentration in DAF (ppb)	On-Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Phenanthrene/Anthracene	168	63	99.97	52.8
Methyl phenanthrene (250)	72	27	N	T
Methyl phenanthrene (251)	80	30	N	T
1-Methyl anthracene	27	10	99.98	T
2-Methyl anthracene	27	10	99.99	T
C_2-Phenanthrene/ Anthracene (262)	5	2	N	ND
C_2-Phenanthrene/ Anthracene (264)	5	2	N	ND
C_2-Phenanthrene/ Anthracene (265)	16	6	N	ND
C_2-Phenanthrene/ Anthracene (267)	37	14	N	ND
C_2-Phenanthrene/ Anthracene (268)	40	15	N	ND
C_2-Phenanthrene/ Anthracene (272)	11	4	N	ND
Fluorene	27	10	N	ND
Methyl fluorene (214)	29	11	99.95	ND
Methyl fluorene (216)	35	13	99.93	T
Methyl fluorene (218)	16	6	99.91	ND
Acenaphthene	3	1	I	ND
Methyl acenaphthene (186)	35	13	N	ND
Methyl acenaphthene (190)	24	9	N	ND
Methyl acenaphthene (193)	16	6	N	ND
Biphenyl	24	9	T(N)	T
Methyl biphenyl (164)	19	7	T(N)	ND
Methyl biphenyl (167)	11	4	T(N)	
Pyrene	29	11	99.88	76.1
$C_{17}H_{12}$ PNA (such as methyl pyrene) (287)	11	4	99.67	ND
Chrysene	5	2	99.69	ND
1,2-Benzanthracene	13	5	99.65	ND

[a] Neutral DAF fraction diluted 100 times.

[b] Neutral fraction of the final clarifier effluent.

N	Noisy, possibly due to unresolved interfering organics
T	Trace
ND	Not detectable

Table 3.8. Comparison of Percent Removal by Activated-Sludge and Activated-Carbon Units for Various Classes of Organic Compounds

Compound Class	Concentration Range in DAF Effluent (ppb)	Percent Removal Range by Activated-Sludge Unit	Average Percent Removal by Activated-Sludge Unit	Percent Removal Range by Activated-Carbon Unit	Average Percent Removal by Activated-Carbon Unit
Alkanes	11-683 (27)	99.33-99.98	99.65 (25)	58.8-97.9	83.5 (18)
n-Alkanes	11-683 (21)	99.33-99.98	99.58 (19)	70.2-97.9	85.9 (15)
Branched Alkanes	67-246 (6)	99.73-99.96	99.88 (6)	58.8-78.7	71.9 (3)
Cycloalkanes	21-71 (10)	99.76-99.98	99.81 (10)	NM	NM
Alkylated Benzenes	5-187 (23)	99.94-99.99	99.97 (18)	44.9-77.3	66.5 (8)
Toluene	101 (1)	99.87	99.87 (1)	84.1	84.1 (1)
C_2-Benzenes	35-187 (3)	99.95-99.97	99.96 (3)	66.7-77.3	73.5 (3)
C_3-Benzenes	5-176 (7)	99.94-99.98	99.97 (6)	44.9-71.2	58.7 (3)
C_4-Benzenes	8-64 (12)	99.96-99.99	99.98 (8)	51.4	51.4 (1)
Alkylated Indans, Tetralins	11-104(18)	99.93-99.99	99.98 (10)	50.0	50.0 (1)
Alkylated Naphthalenes	21-448	99.69-99.99	99.93 (20)	12.0-69.8	49.4 (13)
Naphthalene	197	99.99	99.99 (1)	37.7	37.7 (1)
Methyl Naphthalenes	259-448	99.99-99.99	99.99 (2)	33.3-44.9	39.1 (2)
C_2-Naphthalenes	45-267	99.94-99.98	99.98 (6)	12.0-55.8	34.1 (5)
C_3-Naphthalenes	21-160	99.69-99.97	99.89 (11)	45.2-69.8	71.1 (5)
Alkylated Benzothiophenes & Dibenzothiophenes	8-32	99.81-99.93	99.88 (8)	71.4-82.9	77.1 (2)
Alkylated PNAs	3-168	99.65-99.99	99.86 (10)	52.8-76.1	64.5 (2)

NM Not measurable
( ) Number of compounds

sludge of organics is greatest with aromatic compounds and relatively low with nonaromatic compounds. On the other hand, with activated carbon, greatest removal is with nonaromatic compounds. A striking example of this can be seen by looking at the raw data stored on disc (Table 3.9). In this table, the actual counts (or relative current generated by ions hitting the electron multiplier of the mass spectrometer) are recorded for 57, 97, and 142 AMUs for the final-clarifier effluent and the activated-carbon effluent. The 57 ion is typically used to look at alkanes, the 97 ion for cycloalkanes (and alkanes) and the 142 ion, here specifically for 2-methyl naphthalene (the first peak) and 1-methyl naphthalene (the second peak). The data are tabulated for successive scans and the 62 scans represent a little less than two minutes in the GC/MS run. It can be seen that the 142 peak for the final-clarifier fraction rises to 100 and then drops off and again rises to 55 and drops off, while in the activated-carbon fraction, the 142 ion rises to 69 and then drops off and again rises to 28 and drops off. One can visually inspect these data and see that there is only about a 30% removal for 2-methyl naphthalene and a 50% removal for 1-methyl naphthalene. Conversely, compared to the final clarifier, there are very large removals of alkanes (57) and cycloalkanes (97) by the activated carbon. In fact, looking at the raw data, one gets the impression that the activated carbon has adsorbed most of the organics and many of the organics that cannot be identified directly in the final clarifier because they are there in very small quantities. By adding up all the actual counts on the page, one can get a picture of what is happening. With ion 57, there are 15975 counts in the FC fraction and 449 counts in the AC fraction. This represents a "removal" of 97.2% of the 57 ion, presumably alkanes. With the 97 ion, there is a "removal" of 98.0%, representing cycloalkanes (and alkanes). These values are probably fairly representative of how effective the activated carbon is in removing organics. It seems to be relatively more effective in removing the nonaromatic compounds than aromatic compounds of the neutral fraction.

3.2 ACID-FRACTION ORGANIC COMPOUNDS

Over thirty phenols were found in the acid fraction of the DAF effluent. Also, several neutral compounds, which were present in large quantities in neutral fraction, were found in the acid fraction apparently due to incomplete separation during the extraction. A listing of compounds found in the

Table 3.9. Raw Data Output from GC/MS data System of 57, 97 and 142 ions Demonstrating the Pronounced Removal by the Activated Carbon of Alkanes (57 Ion) and Cycloalkanes (97 Ion) and Only Partial Removal of Methyl Naphthalenes (142 Ion)

Spectrum No.	Final Clarifier Effluent (Neutral Fraction)						Activated Carbon Effluent (Neutral Fraction)					
	Ion Counts/ 57 Ion		Ion Counts/ 97 Ion		Ion Counts/ 142 Ion		Ion Counts/ 57 Ion		Ion Counts/ 97 Ion		Ion Counts/ 142 Ion	
992	57-	110	97-	60	142-	0	57-	0	97-	0	142-	0
993	57-	130	97-	58	142-	0	57-	8	97-	0	142-	0
994	57-	139	97-	62	142-	0	57-	6	97-	0	142-	0
995	57-	132	97-	55	142-	0	57-	0	97-	0	142-	0
996	57-	131	97-	85	142-	0	57-	0	97-	0	142-	0
997	57-	221	97-	73	142-	11	57-	0	97-	0	142-	0
998	57-	375	97-	68	142-	0	57-	9	97-	0	142-	12
999	57-	543	97-	84	142-	29	57-	0	97-	0	142-	27
1000	57-	510	97-	98	142-	58	57-	0	97-	0	142-	56
1001	57-	350	97-	61	142-	100	57-	21	97-	0	142-	69
1002	57-	222	97-	54	142-	78	57-	11	97-	0	142-	50
1003	57-	147	97-	55	142-	99	57-	11	97-	0	142-	0
1004	57-	151	97-	75	142-	53	57-	19	97-	0	142-	24
1005	57-	131	97-	76	142-	45	57-	12	97-	0	142-	9
1006	57-	150	97-	89	142-	25	57-	0	97-	0	142-	14
1007	57-	128	97-	53	142-	27	57-	6	97-	10	142-	10
1008	57-	131	97-	62	142-	0	57-	0	97-	0	142-	0
1009	57-	98	97-	75	142-	0	57-	0	97-	0	142-	11
1010	57-	130	97-	77	142-	14	57-	0	97-	0	142-	6
1011	57-	188	97-	64	142-	0	57-	0	97-	7	142-	0
1012	57-	366	97-	58	142-	0	57-	0	97-	0	142-	0
1013	57-	602	97-	71	142-	0	57-	0	97-	0	142-	0
1014	57-	508	97-	81	142-	0	57-	0	97-	0	142-	0
1015	57-	293	97-	70	142-	0	57-	9	97-	0	142-	0
1016	57-	155	97-	79	142-	0	57-	21	97-	0	142-	7
1017	57-	90	97-	77	142-	0	57-	10	97-	0	142-	0
1018	57-	128	97-	81	142-	0	57-	0	97-	6	142-	0
1019	57-	163	97-	55	142-	0	57-	0	97-	0	142-	0
1020	57-	186	97-	72	142-	0	57-	0	97-	0	142-	0
1021	57-	245	97-	62	142-	0	57-	0	97-	0	142-	0
1022	57-	600	97-	88	142-	0	57-	14	97-	0	142-	0
1023	57-	1314	97-	109	142-	0	57-	8	97-	0	142-	0
1024	57-	1654	97-	120	142-	0	57-	18	97-	9	142-	0
1025	57-	1123	97-	96	142-	0	57-	35	97-	9	142-	0
1026	57-	382	97-	54	142-	0	57-	37	97-	0	142-	0
1027	57-	156	97-	55	142-	0	57-	33	97-	6	142-	0
1028	57-	164	97-	49	142-	0	57-	21	97-	0	142-	0
1029	57-	222	97-	54	142-	0	57-	18	97-	0	142-	0
1030	57-	232	97-	54	142-	0	57-	7	97-	0	142-	15
1031	57-	148	97-	48	142-	22	57-	7	97-	0	142-	13
1032	57-	142	97-	58	142-	28	57-	7	97-	0	142-	44
1033	57-	152	97-	56	142-	45	57-	11	97-	0	142-	28
1034	57-	167	97-	71	142-	55	57-	8	97-	7	142-	0
1035	57-	183	97-	72	142-	52	57-	0	97-	0	142-	18
1036	57-	256	97-	84	142-	21	57-	12	97-	0	142-	18
1037	57-	271	97-	87	142-	19	57-	10	97-	0	142-	16
1038	57-	232	97-	75	142-	18	57-	8	97-	0	142-	0
1039	57-	159	97-	62	142-	21	57-	6	97-	0	142-	0
1040	57-	172	97-	0	142-	0	57-	8	97-	0	142-	0
1041	57-	110	97-	87	142-	0	57-	0	97-	0	142-	7
1042	57-	132	97-	98	142-	0	57-	10	97-	0	142-	0
1043	57-	127	97-	114	142-	0	57-	9	97-	6	142-	0
1044	57-	157	97-	147	142-	0	57-	12	97-	0	142-	0
1045	57-	183	97-	207	142-	0	57-	0	97-	10	142-	0
1046	57-	181	97-	251	142-	15	57-	7	97-	0	142-	0
1047	57-	208	97-	148	142-	0	57-	0	97-	8	142-	0
1048	57-	145	97-	102	142-	0	57-	0	97-	8	142-	0
1049	57-	97	97-	86	142-	0	57-	0	97-	9	142-	0
1050	57-	143	97-	97	142-	0	57-	6	97-	0	142-	0

acid fraction of the DAF effluent can be found in Appendix B. It can be seen that, along with phenol itself, there are cresols, xylenols, ethyl phenols, C_3-phenols, C_4-phenols, and an unidentified plasticizer. The predominant phenols are phenol, the cresols, an unidentified xylenol, and 2,3-xylenol.

In Table 3.10, the approximate concentration in the acid fraction of the DAF effluent of these phenols is listed, along with percent removal by the activated sludge and activated carbon. The range of concentration in the DAF effluent is from below 1 ppb to about 50 ppb. Because of the extremely low concentrations of these phenols, it was difficult to find any phenols in the final-clarifier or activated-carbon effluents. Removal by activated sludge for three alkylated phenols was in the range of 99.89-99.98%. Most likely, the other phenols were practically completely degraded by the activated sludge. This is not unexpected, since phenols are oxidized readily not only by bacteria but also by oxygen, which was continuously fed into the activated-sludge unit. No evidence of the intermediates, such as quinones, was found in the neutral fraction of the final-clarifier effluent. With the great efficiency of removal of phenols by the activated-sludge unit, it was, of course, impossible to find any trace of phenols in the activated-carbon effluent. Thus, a measurement of percent removal by the activated carbon was not possible.

3.3 BASE-FRACTION ORGANIC COMPOUNDS

Over 70 compounds were found in the base fraction of the DAF effluent (Appendix C), several of which were not organic bases. Extraneous organics included those compounds present in large quantities in the neutral fraction of the DAF effluent, which apparently were not separated completely in the extraction process. In addition, there were considerable quantities of phenol and alkylated phenols such as cresols, ethyl phenol, and xylenols. These compounds probably formed acid salts with many of the organic bases present in the DAF effluent and were carried into the base fraction during extraction. This salt formation can sometimes cause problems during a GC/MS run. If the salts decompose during standing, or in the hot injection port, the retention time is not altered. If, however, decomposition takes place on the column or in the transfer line to the mass spectrometer, results are unpredictable.

Table 3.10. Phenols in the Acid Fraction of the DAF Effluent and Percent Removal by the Activated Sludge and Activated Carbon Units (50-m OV-17 Column, 3 μL Injection)

Compound (Number)	Concentration in DAF (ppb)	On Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Phenol	22	83	ND	ND
Cresol (2)	33	124	99.98	NM
p-Cresol	50	186	ND	ND
Ethyl phenol (6)	4	16	ND	ND
Ethyl phenol (10)	7	26	ND	ND
Dimethyl phenol (7)	29	109	ND	ND
2,3-Dimethyl phenol (9)	16	61	99.98	ND
Dimethyl phenol (13)	8	30	ND	ND
n-Propyl phenol (11)	1	5	ND	ND
i-Propyl phenol (5)	2	8	ND	ND
i-Propyl phenol (12)	4	15	ND	ND
i-Propyl phenol (14)	10	37	ND	ND
i-Propyl phenol (15)	1	3	ND	ND
i-Propyl phenol (16)	1	4	ND	ND
n-Propyl phenol & methyl ethyl phenol (19,20)	4	16	ND	ND
n-Propyl phenol & methyl ethyl phenol (22,23)	<1	1	ND	ND
Methyl ethyl phenol (17)	2	9	ND	ND
Methyl ethyl phenol (18)	3	12	ND	ND
2,4,5-Trimethyl phenol	3	10	99.89	ND
Methyl ethyl phenol & C_4-phenol (24,25)	1	4	ND	ND
Methyl ethyl phenol & C_4-phenol (27,28)	<1	2	ND	ND
C_3 and C_4-phenol (31,32)	1	3	ND	ND
C_3 and C_4-phenol (34,35)	1	3	ND	ND
Diethyl phenol (21)	1	3	ND	ND
Diethyl phenol (36)	<1	2	ND	ND

[a] Acid DAF fraction diluted 10 times.

[b] Acid fraction of the final clarifier effluent.

ND Not detectable
NM Not measurable

It was found that there was a variety of very small amounts of alkylated pyridines such as picolines, ethyl pyridines, lutidines, ethyl picolines, collidines, and ethyl lutidines and small amounts of alkylated quinolines, C_1, C_2, and C_3's, and appreciable quantities of aniline and alkylated anilines (Tables 3.11, 3.12, 3.13). Although a few isolated values for percent removals by the activated-sludge and the activated-carbon units have been reported, because of the small quantities involved, not much confidence should be placed in the values. It can be said, however, that the activated sludge does reduce the amount of organic bases, but little can be said about the degree of removal.

3.4 TREATMENT-SYSTEM PERFORMANCE DATA

Performance of the full-scale biosystem and the add-on filtration/carbon train for the common wastewater parameters is shown in Tables 3.14 and 3.15, from Pfeffer, Harrison, and Raphaelian (1977). Some values are reported as less-than (<), reflecting lower limits of detectability as a function of the sampling and analytical protocol.

During the study, refinery crude oil throughput was 115,641 BPSD, the water inlet rate from Maumee Bay was 47.3 MGD, and the wastewater-treatment-plant throughput was 8.6 MGD. There were no significant recorded changes in flow through the plant wastewater treatment system, as measured by the biofeed pumping rates (that is, the wastewater influent to the aeration basin). Note that, waste sludge being insignificant, the final-clarifier effluent and biofeed flows were assumed to be equal. Aeration time was of the order of 16-18 hours and mixed-liquor volatile suspended solids concentration in the aeration basin was 4440 mg/L, during the study. Water temperature in the aeration zone averaged 76°F and settleable solids averaged 35% in the aeration zone and 95% on the clarifier recycle.

Table 3.11. Alkylated Pyridines in the Base Fraction of the DAF Effluent and Percent Removal by Activated Sludge and Activated Carbon Units (50-m OV-17 Column, 3 μL Injection)

Compound (Number)	Concentration in DAF (ppb)	On Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Picoline (1)	<1	2	-	-
Ethyl pyridine (5)	<1	2	ND	ND
4-Ethyl pyridine (8)	<1	2	92.6	ND
Lutidine (4)	<1	2	ND	T
Lutidine (7)	2	9	97.6	ND
Ethyl picoline (9)	NM	NM	NM	ND
2-Ethyl picoline (17)	1	4	ND	ND
Ethyl picoline (36)	6	24	ND	ND
2,4,6-Collidine (14)	2	8	ND	ND
2,3,6-Collidine (16)	<1	2	ND	ND
2,3,5-Collidine (18)	<1	1	ND	ND
Collidine (28)	<1	2	67.0	99.6
Collidine (38)	2	9	ND	ND
C_3-Pyridine (27)	<1	2	ND	ND
C_3-Pyridine (29)	<1	1	ND	ND
Ethyl lutidine (20)	1	4	ND	ND
Ethyl lutidine (22)	<1	1	ND	ND
Ethyl lutidine (24)	1	4	ND	ND
Ethyl lutidine (26)	<1	<1	ND	ND
Ethyl lutidine (49)	<1	2	ND	ND

[a] Base DAF fraction diluted 10 times.

[b] Base fraction of the final clarifier effluent.

NM Not measurable due to interferences
ND Not detectable
T Trace

Table 3.12. Alkylated Quinolines in the Base Fraction of the DAF Effluent and Percent Removal by Activated Sludge and Activated Carbon Units (50-m OV-17 Column, 3 μL Injection)

Compound (Number)	Concentration in DAF (ppb)	On Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Quinoline (45)	6	23	ND	ND
Methyl quinoline (50)	4	16	ND	ND
Methyl quinoline (51)	1	4	ND	ND
Methyl quinoline (52)	<1	2	ND	ND
Methyl quinoline (54)	<1	2	85.1	ND
Methyl quinoline (56)	2	8	ND	ND
Methyl quinoline (58)	1	4	ND	ND
Ethyl quinoline (55)	<1	2	ND	ND
Dimethyl quinoline (62)	2	6	93.6	88.9
Dimethyl quinoline (63)	1	4	ND	ND
Dimethyl quinoline (65)	2	6	ND	ND
Dimethyl quinoline (67)	<1	2	ND	ND
Dimethyl quinoline (68)	2	6	91.9	ND
Dimethyl quinoline (69)	1	4	ND	ND
C_3-Quinoline (71)	2	6	96.8	ND
C_3-Quinoline (72)	2	6	96.7	ND

[a] Base DAF fraction diluted 10 times.

[b] Base fraction of the final clarifier effluent.

ND Not detectable

Table 3.13. Alkylated Anilines in Base Fraction of the DAF Effluent and Percent Removal by Activated Sludge and Activated Carbon Units (50-m OV 17 Column, 3 μL Injection)

Compound (Number)	Concentration in DAF (ppb)	On Column Concentration (ng)[a]	Percent Removal by Activated Sludge[b]	Percent Removal by Activated Carbon
Aniline (23)	27	101	99.5	T
o-Toluidine (31)	29	109	NM	ND
Toluidine (33)	10	38	NM	ND
N,N-Dimethyl aniline (25)	<1	2	88.6	ND

[a] Base DAF fraction diluted 100 times.

[b] Base fraction of the final clarifier effluent.

T Trace
ND Not detectable
NM Not measurable due to interferences

Table 3.14. Daily Performance for Common Wastewater Parameters[a]

	mg/L Intake				mg/L DAF Effluent				mg/L FC Effluent			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Oil and Grease	<10	<10	<10	10	22	33	21	22	<10	<10	<10	<10
Cyanide	<0.02	<0.02	<0.02	<0.02	0.19	0.25	0.31	--	0.16	0.12	0.20	0.10
Phenol	0.03	<0.01	0.03	0.01	3.2	2.6	5.2	4.5	0.02	0.01	0.04	0.02
COD	<15	18	<15	<15	122	172	154	154	49	50	51	44
BOD	<10	<10	14	10	82	127	108	96	<10	15	21	24
TOC	19	19	17	15	39	56	72	60	22	29	27	17
TSS	35	29	11	<10	31	56	37	30	12	<10	<10	<10

	mg/L MMF Effluent				mg/L AC Effluent			
	Day 1	Day 2	Day 3	Day 4	Day 1	Day 2	Day 3	Day 4
Oil and Grease	<10	<10	<10	<10	<10	<10	<10	<10
Cyanide	0.16	0.15	0.20	0.10	<0.02	<0.02	<0.02	<0.02
Phenol	0.02	0.01	0.02	0.02	<0.01	<0.01	<0.01	<0.01
COD	42	38	51	44	<15	<15	<15	<15
BOD	<10	11	22	27	<10	<10	<10	<10
TOC	19	26	23	18	10	12	11	<5
TSS	<10	<10	12	12	<10	<10	<10	<10

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[a] The data of this table were provided by SOHIO's Warrensville, Ohio, Research Center. Rodger McKain (Study Leader), Robert Munko, David Rulison, and Jeffery Smola determined the parameters.

Table 3.15. Average Performance over 4-Day Study Period for Common Wastewater Parameters

	mg/L Intake	mg/L DAF	mg/L FC	mg/L MMF	mg/L AC
Oil & Grease	<10	24	<10	<10	<10
Cyanide	<0.02	0.25	0.14	0.15	<0.02
Phenol	0.02	3.9	0.02	0.02	<0.01
COD	<15	150	48	44	<15
BOD	<10	103	17	17	<10
TOC	18	57	24	22	9
TSS	21	38	<10	<10	<10

REFERENCES

American Society for Testing and Materials, ASTM-D2579, *Total Organic Carbon in Water by Combustion-Infrared Analysis*, ASTM Standards, Pt. 23 (n.d.).

Burlingame, A.L., 1977, *Assessment of the Trace Organic Molecular Composition of Industrial and Municipal Wastewater Effluents by Capillary Gas Chromatography/Real-Time High-Resolution Mass Spectrometry: A Preliminary Report:* Ecotoxicology and Environ. Safety, 1, p. 111-150.

Kim, B.R., et al., 1976, *Influence of activated sludge CRT on adsorption:* Jour. Environ. Eng. Div., Amer. Soc. Civil Eng., v. 102, p. 55-70.

Matthews, J.E., 1978, *Treatment of Petroleum Refinery, Petrochemical, and Combined Industrial-Municipal Wastewaters with Activated Carbon (Literature Review):* R.S. Kerr Environ. Res. Lab., U.S. EPA, Ada, Okla.

Pfeffer, F.M., and W. Harrison and L.A. Raphaelian, 1977, *Organics Reduction Through Add-on Activated Carbon at Pilot Scale:* Proc. Second Open Forum on Management of Petrol. Refinery Wastewater, U.S. EPA, Cincinnati, p. 403-408.

U.S. EPA, 1974, *Manual of Methods for Chemical Analysis of Water and Wastes*, U.S. EPA-625/6-74-003, Cincinnati.

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APPENDIX A

Organic Compounds Found in Neutral Fraction of the Effluent from the Dissolved Air Flotation (DAF) Unit and Their Presence or Absence in the Effluents from the final Clarifier (FC)

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
1	7.0	chloroform	high	+	+
2	7.8	1,1,1-trichloroethane	high	+	+
3	8.3	benzene	medium	+	+
4	8.4	carbon tetrachloride	medium	+	+
5	9.1	cyclohexene	high	+	+
6	13.1	toluene	high	+	+
7	19.7	ethyl benzene	low	+	+
8	20.4	p-xylene	high	+	+
9	20.4	m-xylene	high	+	+
10	22.1	o-xylene	medium	+	+
11	24.3	n-nonane	low	+	-
12	24.9	i-propyl benzene	trace	+	-
13	27.3	n-propyl benzene	low	+	-
14	28.0	m-ethyl toluene	medium	+	-
15	28.2	p-ethyl toluene	medium	+	-
16	28.7	1,3,5-trimethyl benzene	low	+	-
17	29.4	o-ethyl toluene	low	+	T
18	30.65	1,2,4-trimethyl benzene	high	+	+
19	30.8	cycloalkane	low	+	-
20	31.0	cycloalkane	trace	T	-
21	31.75	cycloalkane	low	+	-
22	31.9	i-butyl benzene	trace	+	-
23	32.05	s-butyl benzene	trace	+	-
24	32.65	n-decane	medium	+	-
25	32.7	1,2,3-trimethyl benzene	medium	+	+
26	33.0	m-isopropyl toluene	trace	T	-
27	33.3	o-isopropyl toluene	trace	-	-
28	33.3	p-isopropyl toluene	trace	-	-
29	33.4	indan	medium	+	+
30	33.6		trace		
31	33.95	indene	trace	+	-
32	35.1	m-diethyl benzene	low	T	-
33	35.35	m-n-propyl toluene	low	+	-
34	35.65	p-n-propyl toluene	low	+	-
35	35.7	n-butyl benzene	trace	T	-
36	35.9	1,3-dimethyl-5-ethyl benzene	low	+	-
37	36.4	o-n-propyl toluene	low	+	-
38	37.25	1,4-dimethyl-2-ethyl benzene	low	NM	NM
39	37.25	ethyl styrene	low	-	-
40	37.4	1,3-dimethyl-4-ethyl benzene	low	+	-
41	37.6	ethyl styrene	medium	+	-
42	37.9	1,2-dimethyl-4-ethyl benzene	low	+	-

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
43	38.25	1,3-dimethyl-2-ethyl benzene	low	-	-
44	38.85	cycloalkane	low	+	-
45	39.1	cycloalkane	low	+	-
46	39.3	1,2-dimethyl-3-ethyl benzene	low	T	-
47	39.3	C_5-benzene	trace	NM	NM
48	39.5	C_5-benzene	trace	-	-
49	39.7	cycloalkane	low	+	-
50	40.0	C_5-benzene	trace	-	-
51	40.35	1,2,4,5-tetramethyl benzene	low	+	-
52	40.4	C_5-benzene	trace	-	-
53	40.6	1,2,3,5-tetramethyl benzene	medium	+	+
54	40.6	n-undecane	high	+	-
55	40.85	C_5-benzene	trace	NM	NM
56	41.7	2-methyl indan	medium	T	0
57	42.0	C_5-benzene	trace	-	-
58	42.35	1-methyl indan	medium	+	-
59	42.5	C_5-benzene	trace	-	-
60	42.7	C_5-benzene	trace	+	-
61	42.9	1,2,3,4-tetramethyl benzene	medium	+	-
62	43.05	tetralin	low	-	-
63	43.25	C_5-benzene	trace	+	-
64	43.6	C_5-benzene	trace	+	-
65	43.9	C_5-benzene	trace	-	-
66	44.2	C_5-benzene	trace	+	-
67	44.3	C_5-benzene	trace	-	-
68	44.45	naphthalene	high	+	+
69	44.8	C_5-benzene	low	+	-
70	44.9	C_6-benzene	trace	+	-
71	45.1	C_3-styrene	low	-	-
72	45.55	C_3-styrene	medium	+	-
73	45.6	C_6-benzene	trace	-	-
74	45.75	C_3-styrene	low	+	-
75	46.0	C_5-benzene	trace	T	T
76	46.05	C_6-benzene	trace	T	-
77	46.2	C_3-styrene	medium	T	-
78	46.35	C_6-benzene	trace	+	-
79	46.4		trace	-	-
80	46.6	C_5-benzene	trace	-	-
81	46.7	cycloalkane	trace	+	-
82	46.8		trace	-	-
83	47.0	cycloalkane	low	+	-
84	47.2	C_6-benzene	trace	-	-
85	47.3	C_5-benzene	trace	-	-

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
86	47.4	cycloalkane	low	+	-
87	47.45		trace	-	-
88	47.8	C_5-benzene	low	+	-
89	47.8	C_6-benzene	trace	+	-
90	48.1	C_6 benzene	trace	+	-
91	48.2	n-dodecane	high	+	+
92	48.4		trace	-	-
93	48.6	C_6-benzene	trace	+	-
94	48.7	ethyl indan	low	-	-
95	48.85	C_6-benzene	trace	T	-
96	49.05	C_5-benzene	trace	T	-
97	49.3	C_{13}-alkane	high	+	-
98	49.4		trace	-	-
99	49.7		trace	-	-
100	50.0	dimethyl indan	medium	T	T
101	50.1	C_6-benzene	trace	-	-
102	50.3		trace	-	-
103	50.5	C_6-benzene	trace	-	-
104	50.85	methyl tetralin	medium	T	-
105	51.1	C_6-benzene	trace	T	-
106	51.2	dimethyl indan	low	-	-
107	51.6	C_6-benzene	trace	-	-
108	51.85	C_3-indan	trace	-	-
109	51.9	methyl benzothiophene	low	+	-
110	52.0	C_6-benzene	trace	-	-
111	52.15	dimethyl indan	low	+	-
112	52.2	methyl ethyl indan	trace	-	-
113	52.35	C_6-benzene	trace	-	-
114	52.45	methyl benzothiophene	low	+	+
115	52.55		trace	-	-
116	52.7	2-methyl naphthalene	high	+	+
117	52.8	C_{13}-alkane	medium	+	-
118	52.85	trimethyl indan	trace	-	-
119	53.0	methyl benzothiophene	low	+	-
120	53.1	trimethyl indan	trace	-	-
121	53.35	methyl benzothiophene	low	+	T
122	53.4	trimethyl indan	trace	-	-
123	53.4	C_6-benzene	trace	-	-
124	53.65	C_4-indan/C_3-tetralin	trace	-	-
125	53.7	1-methyl naphthalene	high	+	+
126	53.8	ethyl tetralin	low	+	-
127	54.2	cycloalkane	medium	+	-
128	54.3	C_4-indian/C_3-tetralin	trace	+	-

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
129	54.55	cycloalkane	low	+	-
130	54.55	ethyl tetralin	trace	NM	-
131	54.95	dimethyl tetralin	low	T	-
132	55.05	C_4-indan/C_3-tetralin	trace	T	-
133	55.2	C_6-benzene	trace	-	-
134	55.4	n-tridecane	high	+	+
135	55.45		trace	+	-
136	55.55	C_4-indan/C_3-tetralin	trace	+	-
137	56.4	C_4-indan/C_3-tetralin	trace	-	-
138	56.85	C_4-indan/C_3-tetralin	trace	-	-
139	57.6	C_4-indan/C_3-tetralin	trace	-	-
140	58.15	C_4-indan/C_3-tetralin	low	-	-
141	58.35	biphenyl	low	+	T
142	58.95	C_4-indan/C_3-tetralin	trace	-	-
143	59.1	dimethyl benzothiophene	trace	- +	-
144	59.4	ethyl benzothiophene	trace	+	-
145	59.55	dimethyl benzothiophene	trace	NM	-
146	59.55	ethyl naphthalene	medium	+	+
147	59.95		trace	+	-
148	60.05	dimethyl benzothiophene	low	+	-
149	60.4	dimethyl naphthalene	high	+	+
150	60.6	dimethyl benzothiophene	trace	+	-
151	60.75	C_{14}-alkane	high	+	+
152	61.1	dimethyl benzothiophene	trace	+	-
153	61.15	dimethyl naphthalene	medium	NM	+
154	61.3	dimethyl naphthalene	high	+	+
155	61.5	dimethyl naphthalene	high	+	+
156	61.6	ethyl benzothiophene	trace	+	-
157	62.25	n-tetradecane	high	+	+
158	62.55	dimethyl naphthalene	medium	+	+
159	63.0		low	-	-
160	63.4	dimethyl naphthalene	low	+	+
161	64.75		low	-	-
162	64.95	acenaphthene	trace	+	-
163	65.35		low	-	-
164	65.45	methyl biphenyl	low	+	-
165	65.65		trace	-	-
166	65.8	C_3-naphthalene	low	+	+
167	65.95	methyl biphenyl	low	+	-
168	66.3	C_3-naphthalene	low	+	-
169	66.4	C_{15}-alkane	high	+	+
170	66.5	C_3-naphthalene	trace	+	T
171	66.75	C_{14}-alkane	trace	+	T
172	66.9	C_3-naphthalene	high	+	T

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence (-) (MMF/AC Effluent)
173	67.2	C_3-naphthalene	low	+	-
174	67.45	C_3-naphthalene	low	+	-
175	67.85	C_3-naphthalene	medium	+	-
176	68.05	cycloalkane	trace	+	NM
177	68.25	C_3-naphthalene	medium	+	T
178	68.6	C_3-naphthalene	medium	+	T
179	68.65	n-pentadecane	high	+	+
180	69.45	C_3-naphthalene	medium	+	+
181	69.7	C_3-naphthalene	medium	+	T
182	70.1		low		
183	70.55	C_3-naphthalene	medium	+	T
184	71.15	fluorene	low	NM	NM
185	71.35	C_3-naphthalene	trace	+	-
186	71.7	methyl acenaphthene	low	NM	-
187	71.75	C_3-naphthalene	trace	+	-
188	72.05	C_2-biphenyl	trace	NM	-
189	72.1	methyl acenaphthene	trace	NM	-
190	72.3	methyl acenaphthene	low	NM	-
191	72.6	C_2-biphenyl	trace	+	-
192	72.7	C_4-naphthalene	low	+	-
193	72.8	methyl acenaphthene	low	+	-
194	73.1		trace	-	-
195	73.35		trace	-	-
196	73.7	C_2-biphenyl	trace	NM	-
197	73.9	C_4-naphthalene	trace	T	-
198	74.1		trace	-	-
199	74.45	C_4-naphthalene	trace	NM	-
200	74.5	C_2-biphenyl	trace	+	-
201	74.6	C_4-naphthalene	trace	+	-
202	74.8	n-hexadecane	high	+	+
203	75.0		trace	-	-
204	75.2		trace	-	-
205	75.3	C_4-naphthalene	trace	+	-
206	75.8	C_4-naphthalene	low	+	-
207	76.6	C_4-naphthalene	trace	NM	-
208	77.0	C_4-naphthalene	low	NM	-
209	77.4		trace	-	-
210	77.5		trace	-	-
211	77.85	C_4-naphthalene	low	+	-
212	78.05	C_4-naphthalene	trace	NM	-
213	78.05	C_3-biphenyl	trace	NM	-
214	78.1	methyl fluorene	low	+	-
215	78.35	C_2-acenaphthene	low	NM	-
216	78.4	methyl fluorene	low	+	T

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
217	78.95	C_4-naphthalene	trace	NM	-
218	79.0	methyl fluorene	low	+	-
219	79.05	C_3-biphenyl	trace	NM	-
220	79.1		trace	-	-
221	79.15	C_2-acenaphthene	trace	NM	-
222	79.2	C_4-naphthalene	trace	NM	-
223	79.45	C_2-acenaphthene	trace	NM	-
224	79.55	C_4-naphthalene	trace	NM	-
225	79.75	C_2-acenaphthene	trace	NM	-
226	80.05	C_2-acenaphthene	trace	NM	-
227	80.4	C_3-biphenyl	trace	NM	-
228	80.55	n-heptadecane	high	+	+
229	80.65	dibenzothiophene	low	T	-
230	80.7	C_3-biphenyl	trace	NM	-
231	81.1	pristane	high	+	-
232	81.35		trace	-	-
233	81.8	C_3-biphenyl	trace	NM	-
234	82.2	anthracene/phenanthrene	high	+	+
235	82.95		trace	-	-
236	83.5		trace	-	-
237	83.6		trace	-	-
238	84.05		trace	-	-
239	84.6	C_2-fluorene	low	NM	-
240	84.95	C_2-fluorene	low	NM	-
241	85.3	C_2-fluorene	low	NM	-
242	85.55	C_2-fluorene	trace	NM	-
243	85.9	C_2-fluorene	trace	NM	-
244	86.0	n-octadecane	high	+	+
245	86.25	methyl dibenzothiophene	low	NM	-
246	86.3	C_2-fluorene	trace	NM	-
247	86.75	phytane	medium	+	+
248	86.9	C_2-fluorene	trace	NM	-
249	87.35	methyl dibenzothiophene	low	+	-
250	88.5	methyl phenanthrene	medium	NM	T
251	88.8	methyl phenanthrene	medium	NM	T
252	89.3	methyl phenanthrene	trace	NM	T
253	89.35		trace	-	-
254	89.65	2-methyl anthracene	low	+	T
255	89.95	1-methyl anthracene	low	+	T
256	90.85	C_3 fluorene	trace	+	T
257	91.2	C_3 fluorene	trace	+	-
258	91.3	n-nonadecane	high	+	+
259	91.65		trace	-	-
260	92.4		trace	-	-

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Neutral Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
261	92.65	C_2-dibenzothiophene	trace	-	-
262	93.35	C_2-phenanthrene/anthracene	trace	T	-
263	93.55		trace	-	-
264	94.1	C_2-phenanthrene/anthracene	trace	T	-
265	94.35	C_2-phenanthrene/anthracene	trace	T	-
266	94.4	fluoranthrene	trace	NM	-
267	94.7	C_2-phenanthrene/anthracene	low	+	-
268	95.6	C_2-phenanthrene/anthracene	low	+	-
269	95.9	C_2-phenanthrene/anthracene	trace	T	-
270	96.1	C_2-phenanthracene/anthracene	trace	NM	-
271	96.3	n-eicosane	high	+	+
272	96.5	C_2-phenanthrene/anthracene	trace	NM	-
273	97.2	C_2-phenanthrene/anthracene	trace	NM	-
274	97.4		low	-	-
275	98.8	C_3-phenanthrene/anthracene	trace	T	-
276	98.9	pyrene	low	+	-
277	99.35		trace	-	-
278	99.95	C_3-phenanthrene/anthracene	trace	T	-
279	101.1	n-heneicosane	medium	+	+
280	101.1	C_3-phenanthrene/anthracene	trace	NM	-
281	101.45	C_3-phenanthrene/anthracene	trace	NM	-
282	102.0	C_3-phenanthrene/anthracene	trace	NM	-
283	102.25	C_3-phenanthrene/anthracene	trace	NM	-
284	102.45	$C_{17}H_{12}$ PNA	trace	NM	-
285	103.5	$C_{17}H_{12}$ PNA	trace	T	-
286	104.4	$C_{17}H_{12}$ PNA	trace	NM	-
287	104.7	$C_{17}H_{12}$ PNA	low	+	-
288	105.65	n-docosane	medium	+	+
289	105.7	$C_{17}H_{12}$ PNA	trace	+	-
290	106.05	$C_{17}H_{12}$ PNA	trace	NM	-
291	109.1	$C_{18}H_{14}$ PNA	trace	T	-
292	110.0	n-tricosane	medium	+	+
293	110.0	phthalate	high	+	+
294	110.1	$C_{18}H_{14}$ PNA	trace	T	-
295	110.8		trace	-	-
296	111.2	$C_{18}H_{14}$ PNA	trace	+	-
297	111.45		low	-	-
298	113.9	chrysene	trace	+	-
299	114.2	1,2-benzanthracene	low	+	-
300	114.45	n-tetracosane	low	+	+
301	117.05		trace	-	-
302	118.8		trace	-	-
303	119.75	n-pentacosane	low	+	NM
304	120.0	phthalate	medium	+	+

T Trace
NM Not measurable due to interferences

APPENDIX B

Organic Compounds Found in the Acid Fraction of the Effluent from the Dissolved Air Flotation (DAF) Unit and Their Presence or Absence in the Effluents from the Final Clarifier (FC) and Add-on Mixed-Media Filter/Activated Carbon (MMF/AC) Units

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Acid Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
1	49.0	phenol	medium	-	-
2	51.9	cresol	high	-	-
3	54.3	naphthalene	trace	+	-
4	54.8	p-cresol	high	-	-
5	56.9	i-propyl phenol	trace	-	-
6	57.2	ethyl phenol	low	-	-
7	57.7	dimethyl phenol	medium	-	-
8	58.5	2,4,5-trimethyl phenol	low	+	-
9	60.6	2,3-dimethyl phenol	medium	+	-
10	60.9	ethyl phenol	low	-	-
11	62.2	n-propyl phenol	trace	-	-
12	62.5	i-propyl phenol	low	-	-
13	62.7	dimethyl phenol	low	-	-
14	63.6	i-propyl phenol	low	-	-
15	64.2	i-propyl phenol	trace	-	-
16	64.4	i-propyl phenol	trace	-	-
17	65.4	methyl ethyl phenol	trace	-	-
18	65.9	methyl ethyl phenol	low	-	-
19	66.4	n-propyl phenol	low	-	-
20	66.4	methyl ethyl phenol	low	-	-
21	66.7	diethyl phenol	trace	-	-
22	68.0	n-propyl phenol	trace	-	-
23	68.0	methyl ethyl phenol	trace	-	-
24	68.9	methyl ethyl phenol	trace	-	-
25	68.9	C_4-phenol	trace	-	-
26	69.4	dimethyl naphthalene	trace	-	-
27	69.4	methyl ethyl phenol	trace	-	-
28	69.4	C_4-phenol	trace	-	-
29	70.2	alkene	trace	+	-
30	70.7	dimethyl naphthalene	trace	-	-
31	70.7	C_3-phenol	trace	-	-
32	70.7	C_4-phenol	trace	-	-
33	71.1	dimethyl naphthalene	trace	-	-
34	71.4	C_3-phenol	trace	-	-
35	71.4	C_4-phenol	trace	-	-
36	71.5	diethyl phenol	trace	-	-
37	73.6		trace	-	-
38	76.3	n-heptadecane	trace	+	-
39	77.2	C_6-benzene	trace	+	-
40	82.2	n-octadecane	trace	+	-
41	87.8	n-nonadecane	trace	+	-
42	93.2	n-eicosane	trace	+	-
43	99.4	plasticizer	low	+	+
44	100.0	plasticizer	low	+	+
45	100.4	plasticizer	medium	+	+

APPENDIX C

Organic Compounds Found in the Base Fraction of the Effluent from the Dissolved Air Flotation (DAF) Unit and Their Presence or Absence in the Effluents from the Final Clarifier (FC) and Add-On Mixed-Media Filter/Activated Carbon (MMF/AC) Units

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Base Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
1	22.5	picoline	trace		-
2	23.3		trace		-
3	25.7		trace		-
4	27.2	lutidine	trace	-	T
5	29.3	ethyl pyridine	trace	-	-
6	30.9	C_3-benzene	trace		T
7	31.9	lutidine	low	+	-
8	33.4	4-ethyl pyridine	trace	+	-
9	33.4	ethyl picoline	trace	NM	NM
10	33.7	C_3-benzene	trace	-	-
11	34.5	n-undecane	trace	-	-
12	34.8		trace	-	T
13	35.2		trace	-	-
14	36.2	2,4,6-collidine	trace	-	-
15	36.8	C_3-benzene	trace	-	-
16	37.5	2,3,6-collidine	trace	-	-
17	38.3	2-ethyl picoline	trace	-	-
18	39.6	2,3,5-collidine	trace	-	-
19	40.0		trace	-	-
20	42.0	ethyl lutidine	trace	-	-
21	42.2	n-dodecane	trace	-	-
22	42.2	ethyl lutidine	trace	-	-
23	42.7	aniline	medium	+	T
24	43.6	ethyl lutidine	trace	-	-
25	43.6	N,N-dimethyl aniline	trace	+	-
26	43.9	ethyl lutidine	trace	-	-
27	44.3	C_3-pyridine	trace	-	-
28	45.4	collidine	trace	+	+
29	45.7	C_3-pyridine	trace	-	-
30	46.5		trace	-	-
31	48.9	o-toluidine	medium	NM	-
32	49.2	phenol	low	-	-
33	49.7	toluidine	low	NM	-
34	52.2	p-cresol	low	-	-
35	54.3	naphthalene	trace	-	-
36	55.0	ethyl picoline	low	-	-
37	55.1	cresol	low	-	-
38	55.7	collidine	trace	-	-
39	56.9	n-tetradecane	trace	-	-
40	57.4		trace	-	-

Compound Number	Retention Time (Min)	Compound Name	Relative Concentration in DAF Base Fraction	Presence(+), Absence(-) (FC Effluent)	Presence(+), Absence(-) (MMF/AC Effluent)
41	57.8	xylenol	trace	-	-
42	60.7	xylenol	trace	-	-
43	60.9	xylenol	trace	-	-
44	61.1	ethyl phenol	trace	-	-
45	61.6	quinoline	low	-	-
46	62.2	2-methyl naphthalene	trace	-	-
47	63.7	n-pentadecane	trace	-	-
48	63.9	1-methyl naphthalene	trace	-	-
49	64.3	ethyl lutidine	trace	-	-
50	65.6	methyl quinoline	low	-	-
51	65.8	methyl quinoline	trace	-	-
52	66.9	methyl quinoline	trace	-	-
53	67.6				
54	68.4	methyl quinoline	trace	+	-
55	68.7	ethyl quinoline	trace	-	-
56	69.3	methyl quinoline	trace	-	-
57	69.4	dimethyl naphthalene	trace	-	-
58	69.8	methyl quinoline	trace	-	-
59	70.2	n-hexadecane	trace	-	-
60	70.8	dimethyl naphthalene	trace	-	-
61	71.1	dimethyl naphthalene	trace	-	-
62	71.5	dimethyl quinoline	trace	+	+
63	71.8	dimethyl quinoline	trace	-	-
64	72.4	dimethyl naphthalene	trace	-	-
65	72.9	dimethyl quinoline	trace	-	-
66	73.9	dimethyl naphthalene	trace	-	-
67	74.6	dimethyl quinoline	trace	-	-
68	75.1	dimethyl quinoline	trace	+	-
69	75.5	dimethyl quinoline	trace	-	-
70	76.3	n-heptadecane	trace	-	-
71	78.7	C_3-quinoline	trace	+	-
72	79.6	C_3-quinoline	trace	+	-
73	82.2	n-octadecane	trace	-	-
74	87.8	n-nonadecane	trace	-	-
75	93.2	n-eicosane	trace	-	-
76	97.9	plasticizer	trace	-	-
77	98.2	n-heneicosane	trace	-	-
78	98.6	plasticizer	trace	-	-
79	98.6	alkane	trace	-	-

T Trace
NM Not measurable due to interferences

APPENDIX D

Massgram Plots for Compounds in the Neutral Fraction of the DAF Effluent

Compound Type — Page

Alkylated Benzenes

Toluene, C_2-Benzenes, and C_3-Benzenes D2
C_4-Benzenes D3
C_5-Benzenes D4

Alkylated Indans, Styrenes, and Tetralins

Indans, Ethyl Styrenes, and Tetralin D5
C_2-Indans, C_3-Styrenes, and C_1-Tetralins D6
C_3-Indans and C_2-Tetralins D7

Alkylated Naphthalenes

Naphthalenes, Methyl Naphthalenes, and C_2-Naphthalenes D8
C_3-Naphthalenes D9
C_4-Naphthalenes D10

Alkylated Biphenyls and Acenaphthenes

Biphenyl, Acenaphthene, Methyl Biphenyls, and Methyl Acenaphthenes D11
C_2-Biphenyls and C_2-Acenaphthenes D12

Alkylated Fluorenes

Fluorene D13
Methyl Fluorenes D14
C_2-Fluorenes D15

Alkylated Phenanthrenes and Anthracenes

Phenanthrene, Anthracene, Methyl Phenanthrenes, and Methyl Anthracenes D16
C_2-Phenanthrenes and C_2-Anthracenes D17

Alkylated Pyrenes

Pyrenes and Methyl Pyrenes D18

Miscellaneous PNAs

Chrysene and 1,12-Benzanthracene D19

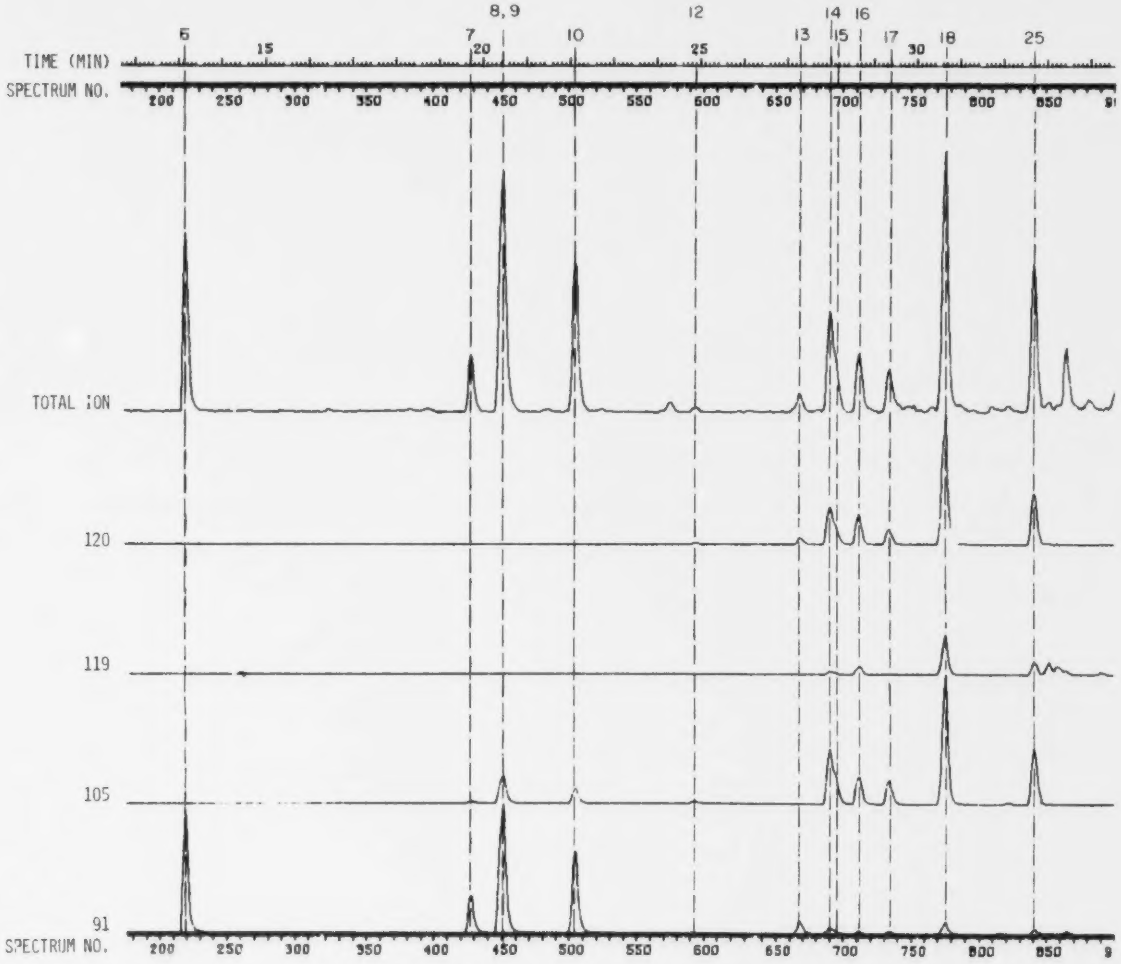
Alkylated Benzothiophenes

C_1-Benzothiophenes D20
C_2-Benzothiophenes D21

Alkylated Dibenzothiophenes

Dibenzothiophene D10
C_1-Dibenzothiophenes D22
Alkanes and Cycloalkanes D23

MASSGRAM PLOTS OF KEY IONS (91, 105, 119, AND 120) FOR IDENTIFYING TOLUENE, C_2-BENZENES, AND C_3-BENZENES



C_1-BENZENES

6 Toluene

C_2-BENZENES

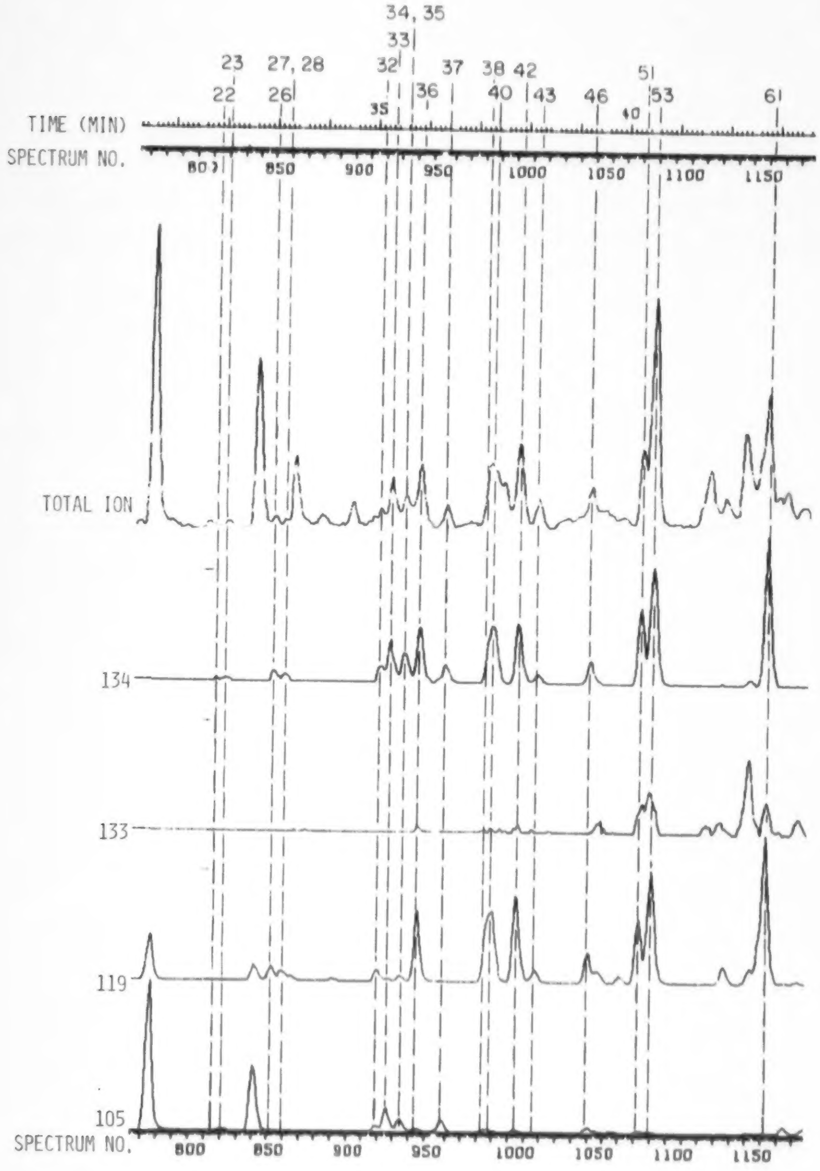
7 Ethyl benzene
8,9 p and m-Xylenes
10 o-Xylene

C_3 BENZENES

12 i-Propyl benzene
13 n-Propyl benzene
14 m-Ethyl toluene
15 p-Ethyl toluene
16 1,3,5-Trimethyl benzene
17 o-Ethyl toluene
18 1,2,4-Trimethyl benzene
25 1,2,3,-Trimethyl benzene

D3

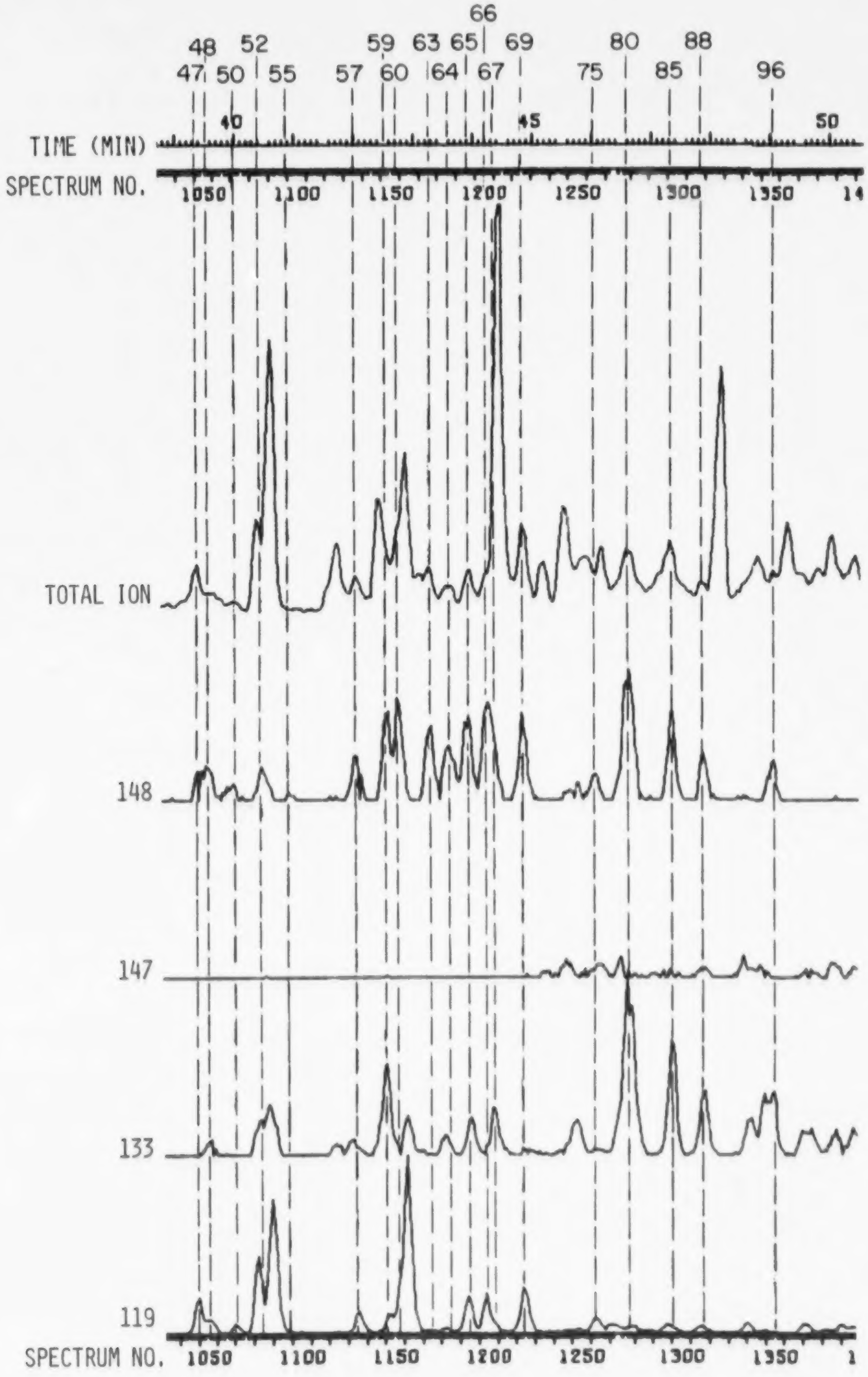
MASSGRAM PLOTS OF KEY IONS (105, 119, 133, 134) FOR IDENTIFYING C_4-BENZENES



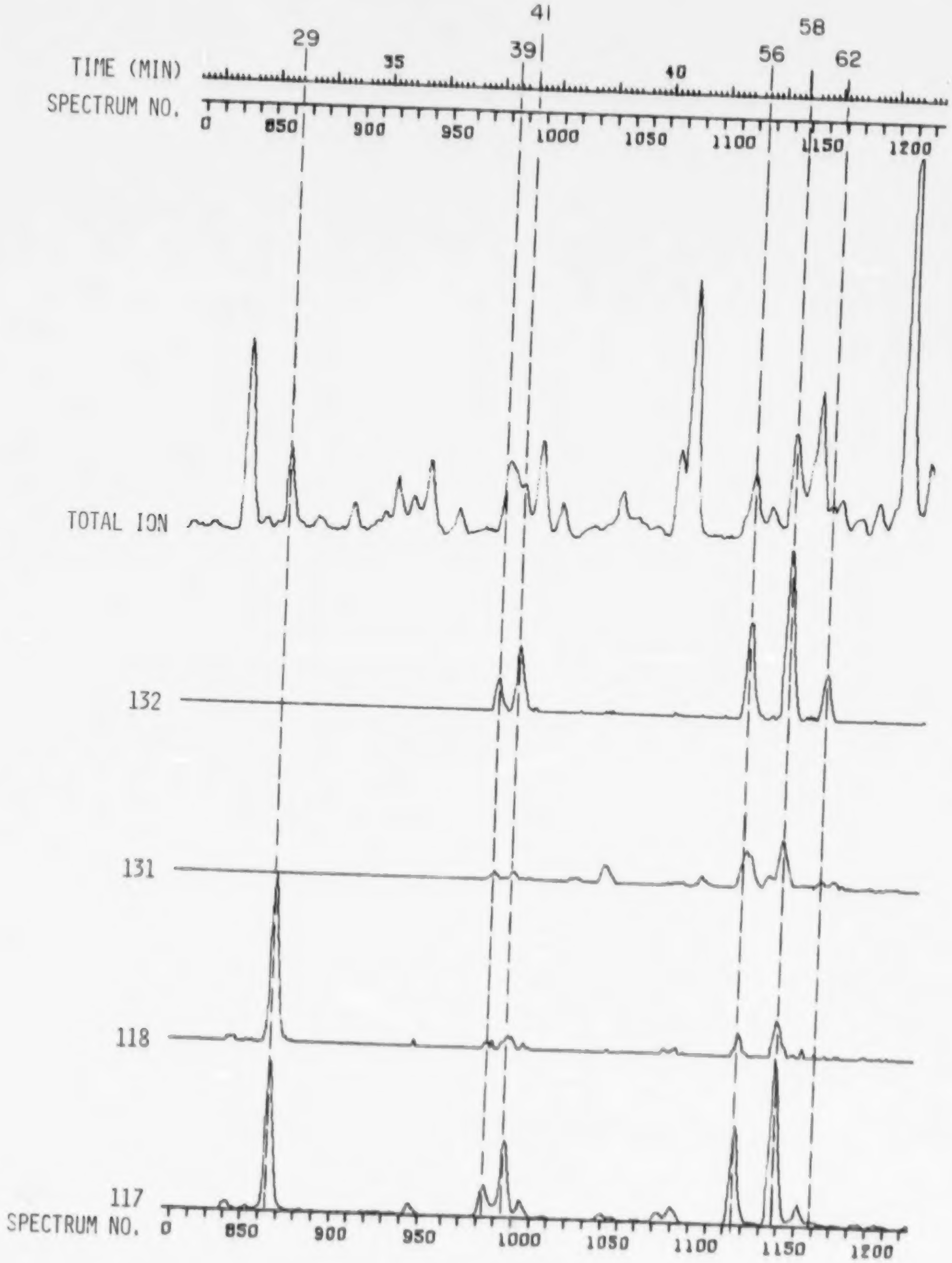
C_4-BENZENES

22	i-Butyl benzene
23	s-Butyl benzene
26	m-Isopropyl toluene
27,28	p and o-Isopropyl toluene
32	m-Diethyl benzene
33	m-n-Propyl toluene
34,35	p-n-Propyl toluene and n-butyl benzene
36	1,3-Dimethyl-5-ethyl benzene
37	o-n-Propyl toluene
38	1,4-Dimethyl-2-ethyl benzene
40	1,3-Dimethyl-4-ethyl benzene
42	1,2-Dimethyl-4-ethyl benzene
43	1,3-Dimethyl-2-ethyl benzene
46	1,2-Dimethyl-3-ethyl benzene
51	1,2,4,5-Tetramethyl benzene
53	1,2,3,5-Tetramethyl benzene
61	1,2,3,4-Tetramethyl benzene

MASSGRAM PLOTS OF KEY IONS (119, 133, 147, 148) FOR IDENTIFYING C$_5$-BENZENES



MASSGRAM PLOTS OF KEY IONS (117, 118, 131, 132) FOR IDENTIFYING INDANS, ETHYL STYRENES, AND TETRALIN



INDANS

29 Indan
56 2-Methyl indan
58 1-Methyl indan

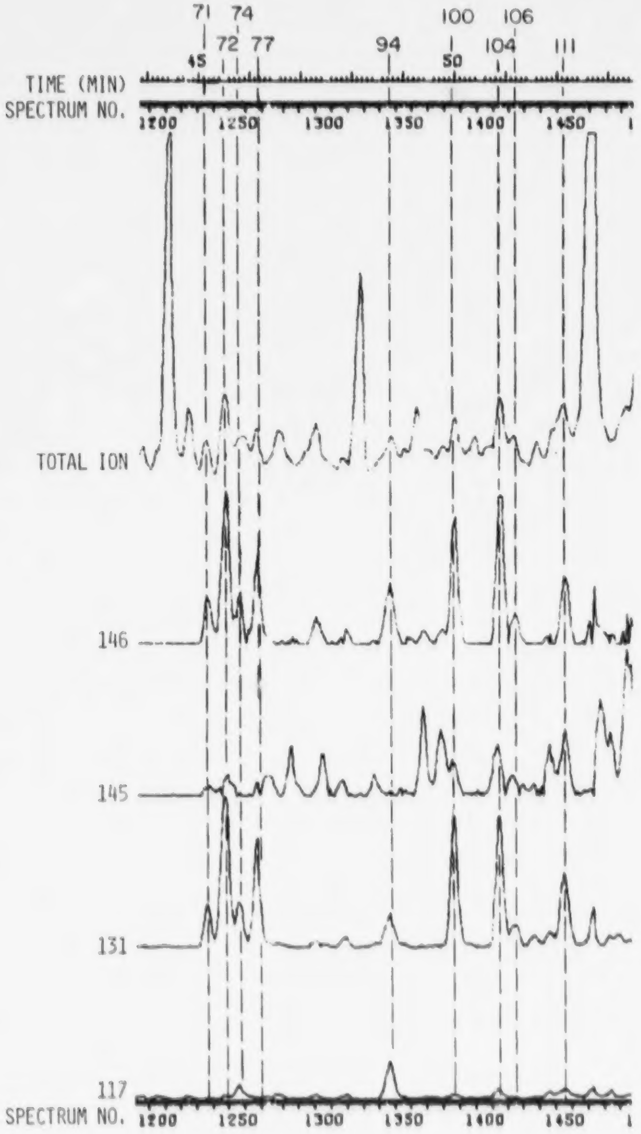
ETHYL STYRENES

39 Ethyl styrene
41 Ethyl styrene

TETRALINS

62 Tetralin

MASSGRAM PLOTS OF KEY IONS (117, 131, 145, 146) FOR IDENTIFYING C_2-INDANS, C_3-STYRENES, AND C_1-TETRALINS



C_2-INDANS

94	Ethyl indan
100	Dimethyl indan
106	Dimethyl indan
111	Dimethyl indan

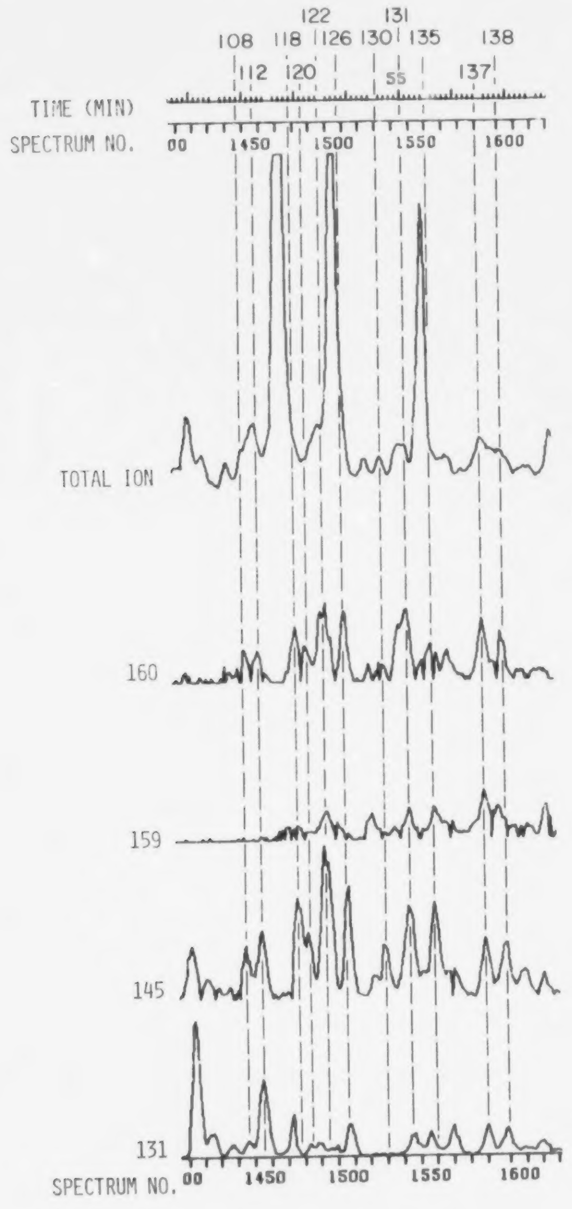
C_3-STYRENES

71	C_3-Styrene
72	C_3-Styrene
74	C_3-Styrene
77	C_3-Styrene

C_1-TETRALINS

104	Methyl tetralin

MASSGRAM PLOTS OF KEY IONS (131, 145, 159, 160) FOR IDENTIFYING C_3-INDANS AND C_2-TETRALINS



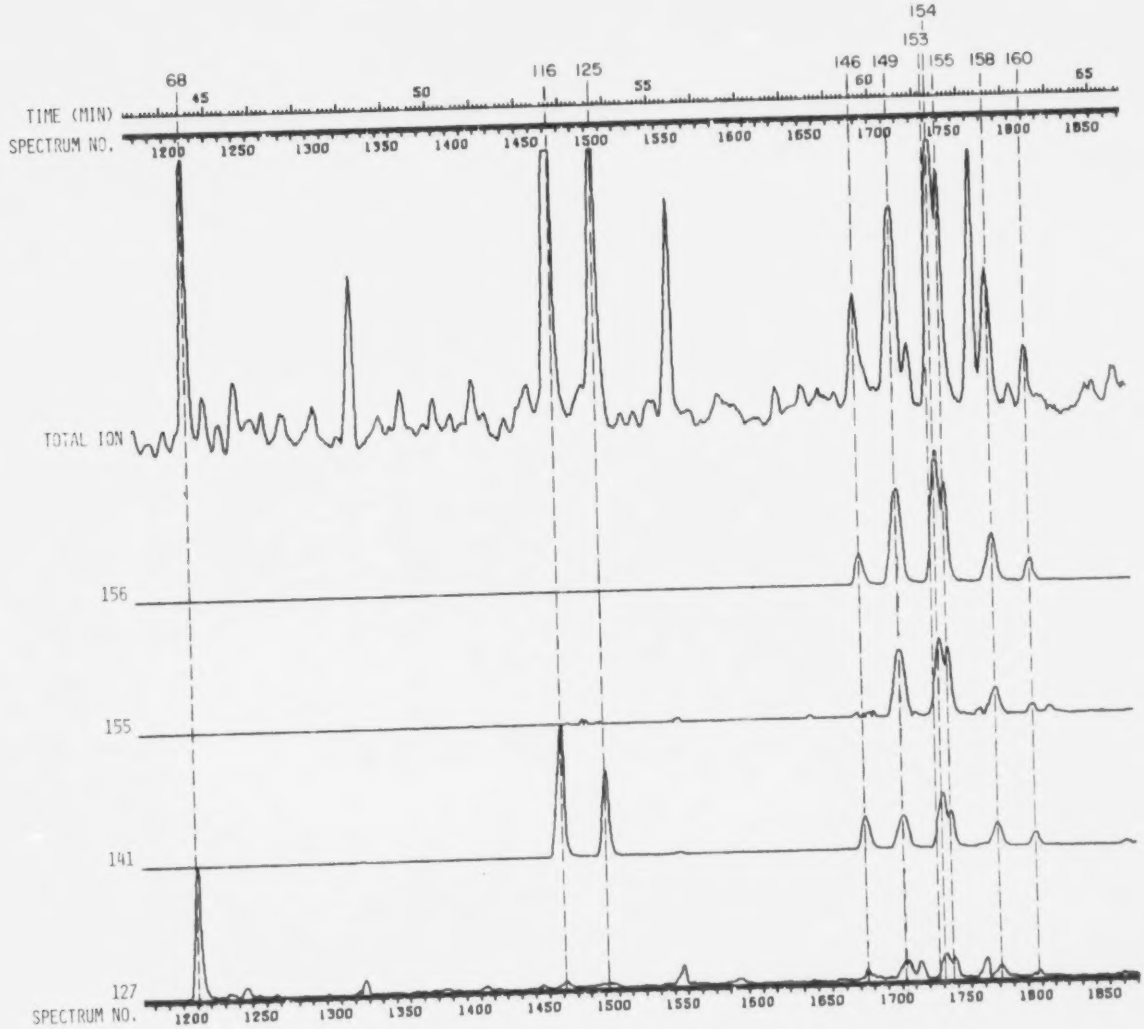
C_3-INDANS

108	C_3-INDAN
112	METHYL ETHYL INDAN
118	TRIMETHYL INDAN
120	TRIMETHYL INDAN
122	TRIMETHYL INDAN

C_2-TETRALINS

126	ETHYL TETRALIN
130	ETHYL TETRALIN
131	DIMETHYL TETRALIN
137	DIMETHYL TETRALIN
138	C_2-TETRALIN

MASSGRAM PLOTS OF KEY IONS (127, 141, 155, 156) FOR IDENTIFYING
NAPHTHALENE, METHYL NAPHTHALENES, AND C_2-NAPHTHALENES



NAPHTHALENE

68 Naphthalene

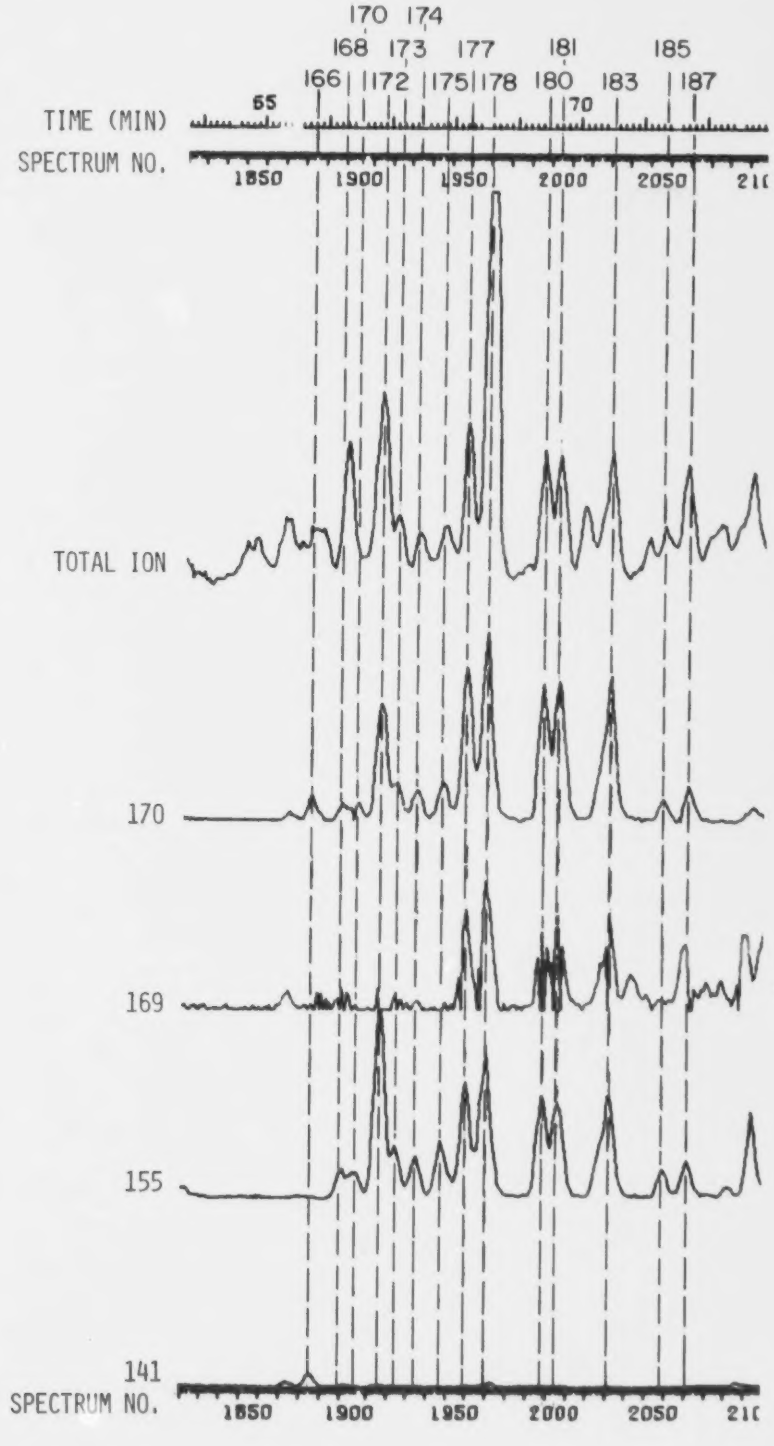
C_1-NAPHTHALENES

116 2-Methyl naphthalene
125 1-Methyl naphthalene

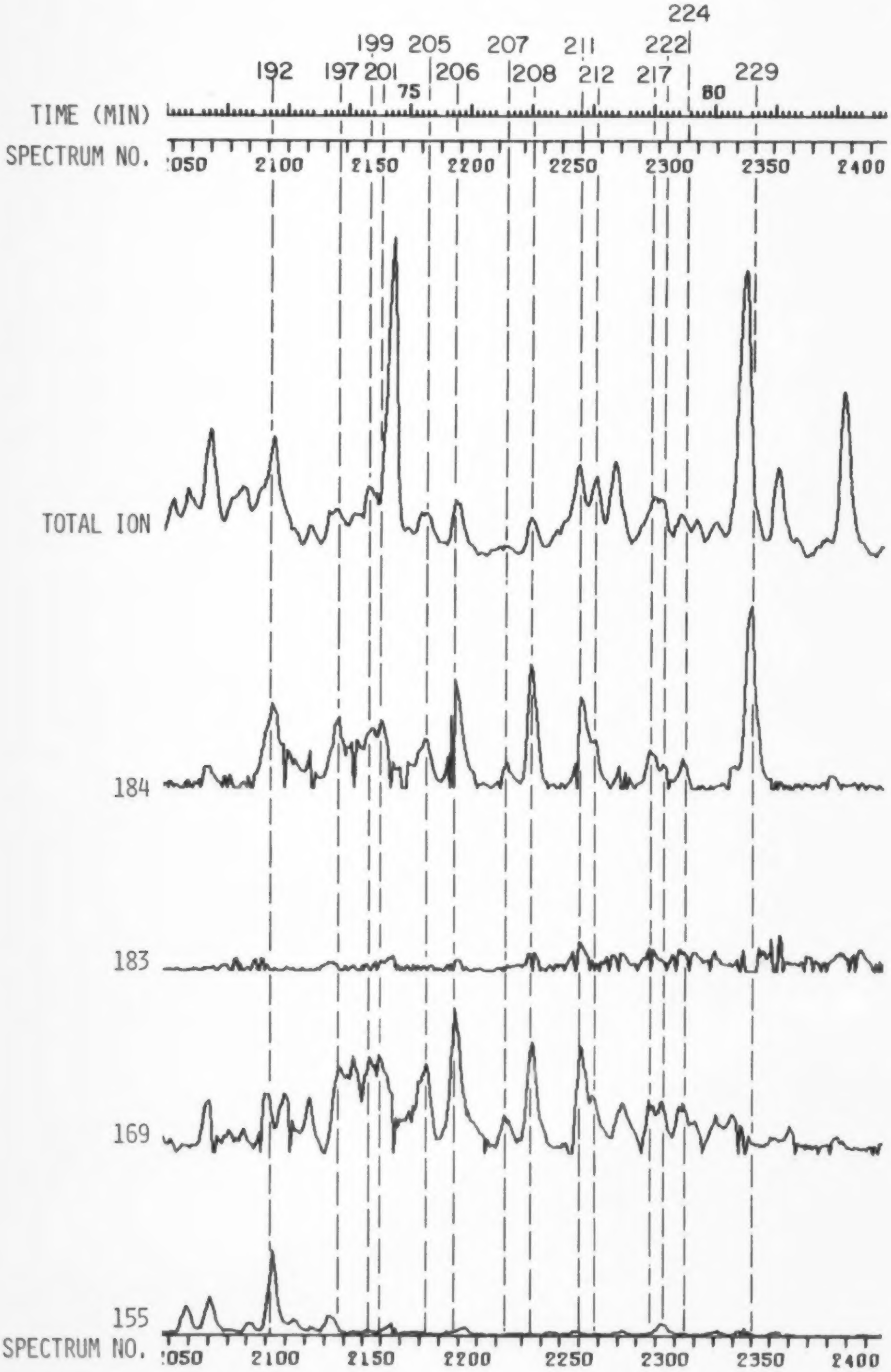
C_2-NAPHTHALENES

146 Ethyl naphthalene
149 Dimethyl naphthalene
153 Dimethyl naphthalene
154 Dimethyl Naphthalene
155 Dimethyl naphthalene
158 Dimethyl naphthalene
160 Dimethyl naphthalene

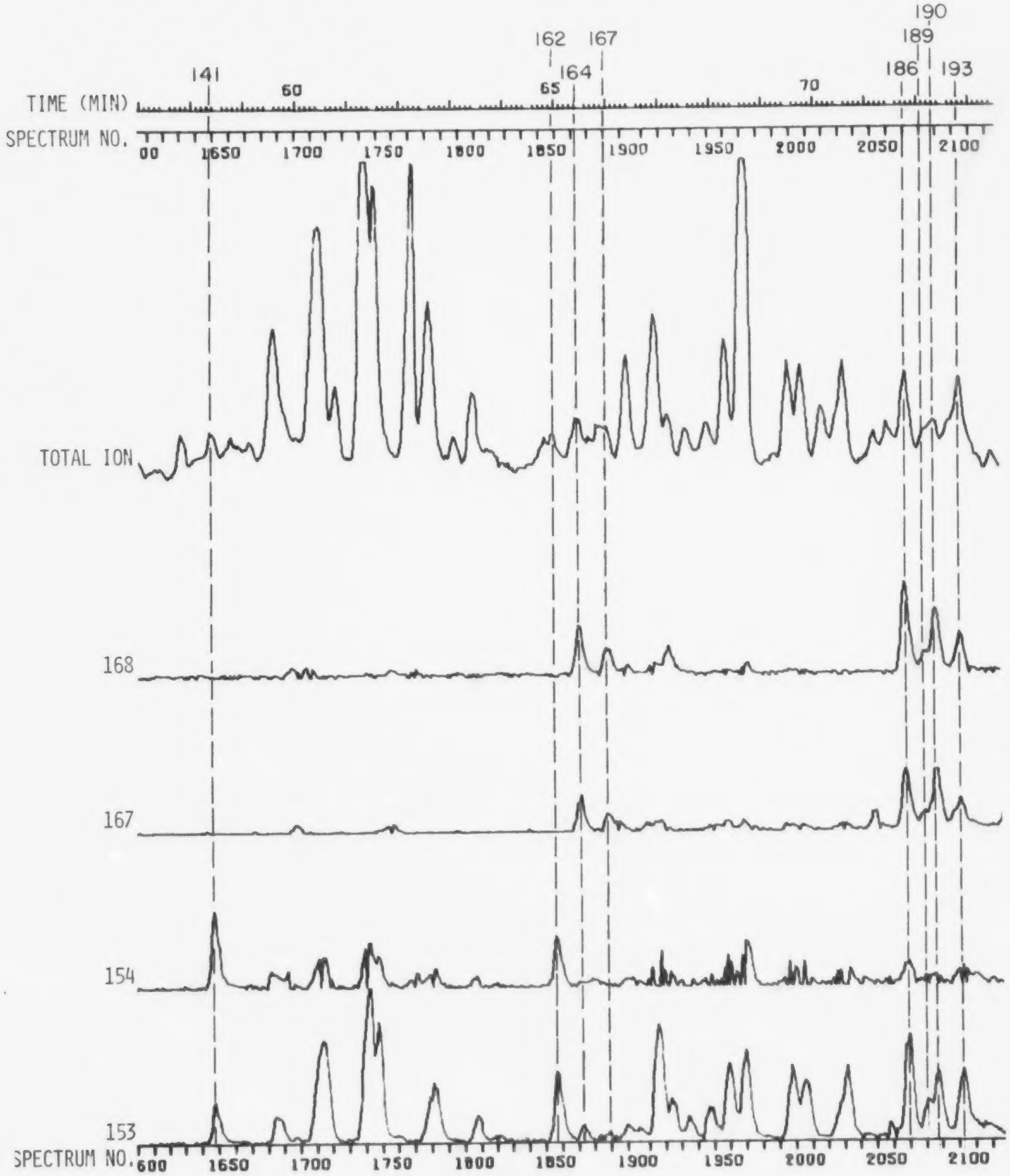
MASSGRAM PLOTS OF KEY IONS (141, 155, 169, 170) FOR IDENTIFYING C_3-NAPHTHALENES



MASSGRAM PLOTS OF KEY IONS (155, 169, 183, 184) FOR IDENTIFYING C_4-NAPHTHALENES AND DIBENZOTHIOPHENE (NUMBER 229)

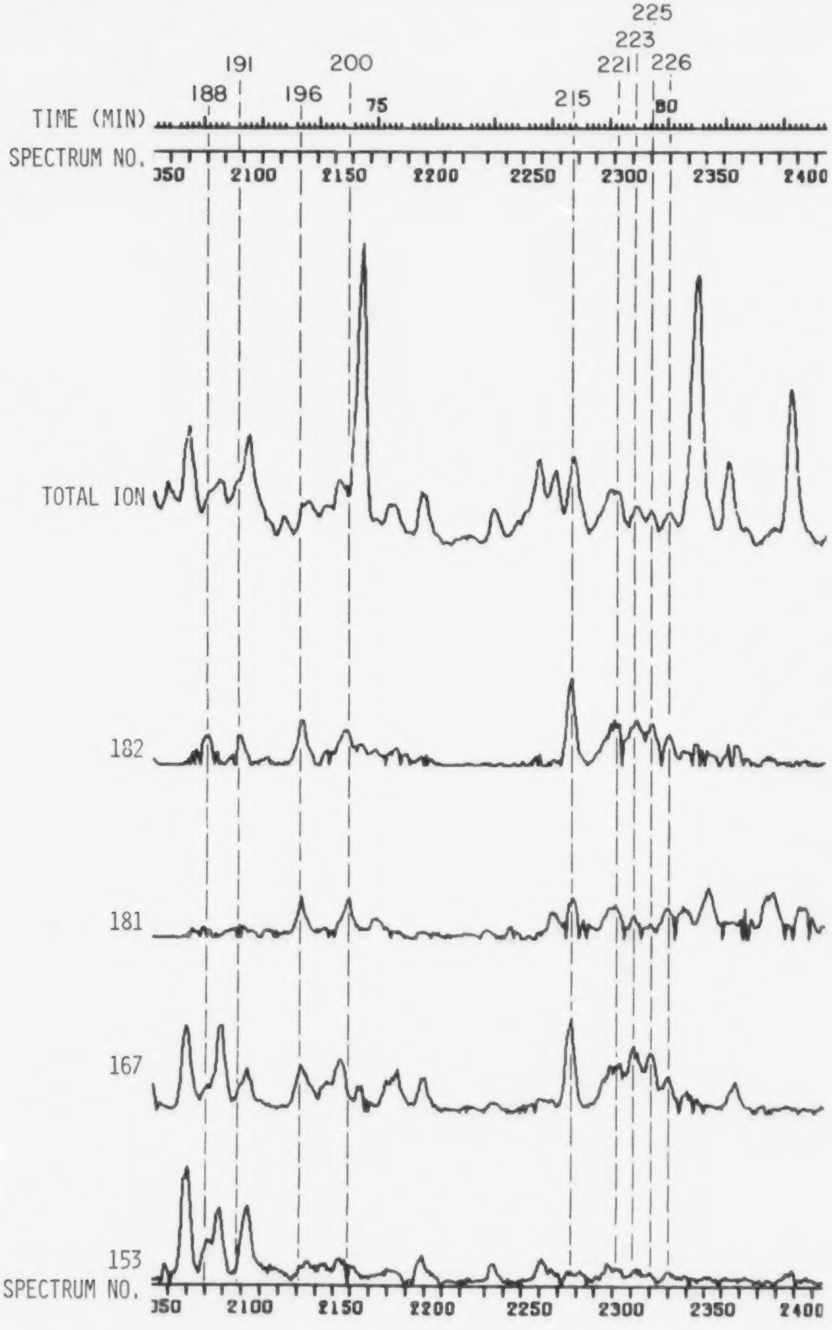


MASSGRAM PLOTS OF KEY IONS (153, 154, 167, 168) FOR IDENTIFYING BIPHENYL, ACENAPHTHENE, METHYL BIPHENYLS, AND METHYL ACENAPHTHENES



BIPHENYL	METHYL BIPHENYLS	ACENAPHTHENE	METHYL ACENAPHTHENES
141	164, 167	162	186, 189, 190, 193

MASSGRAM PLOTS OF KEY IONS (153, 167, 181, 182) FOR IDENTIFYING C_2-BIPHENYLS AND C_2-ACENAPHTHENES



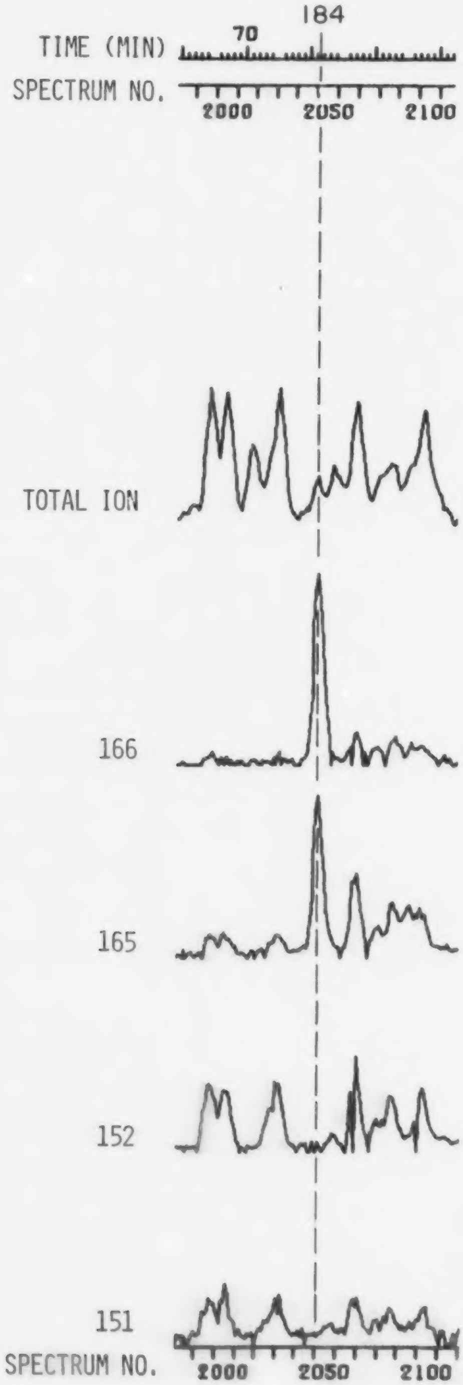
C_2-BIPHENYLS

188, 191, 196, 200

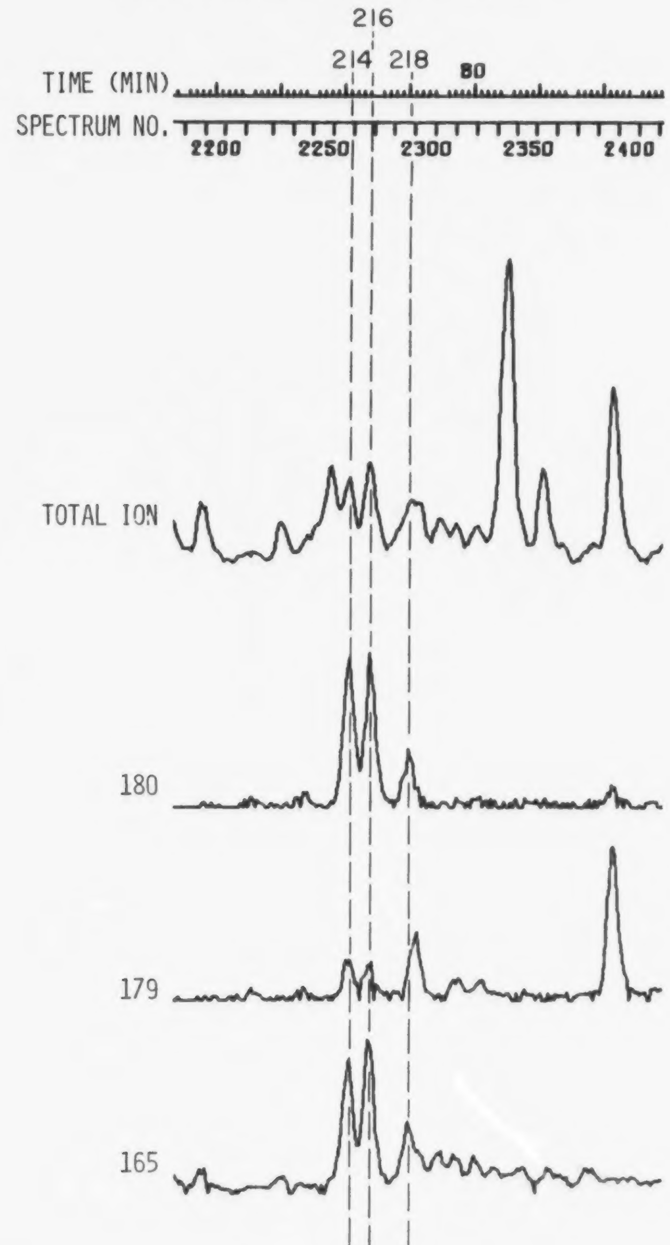
C_2-ACENAPHTHENES

215, 221, 223, 225, 226

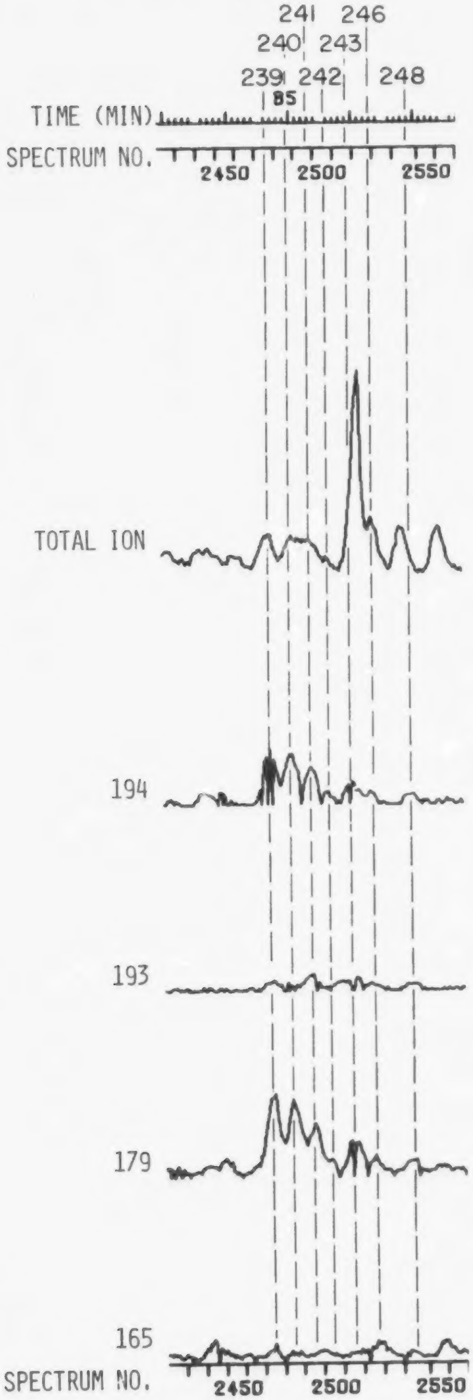
MASSGRAM PLOTS OF KEY IONS
(166, 165) FOR IDENTIFYING
FLUORENE



MASSGRAM PLOTS OF KEY IONS (151, 165, 179, 180) FOR IDENTIFYING METHYL FLUORENES

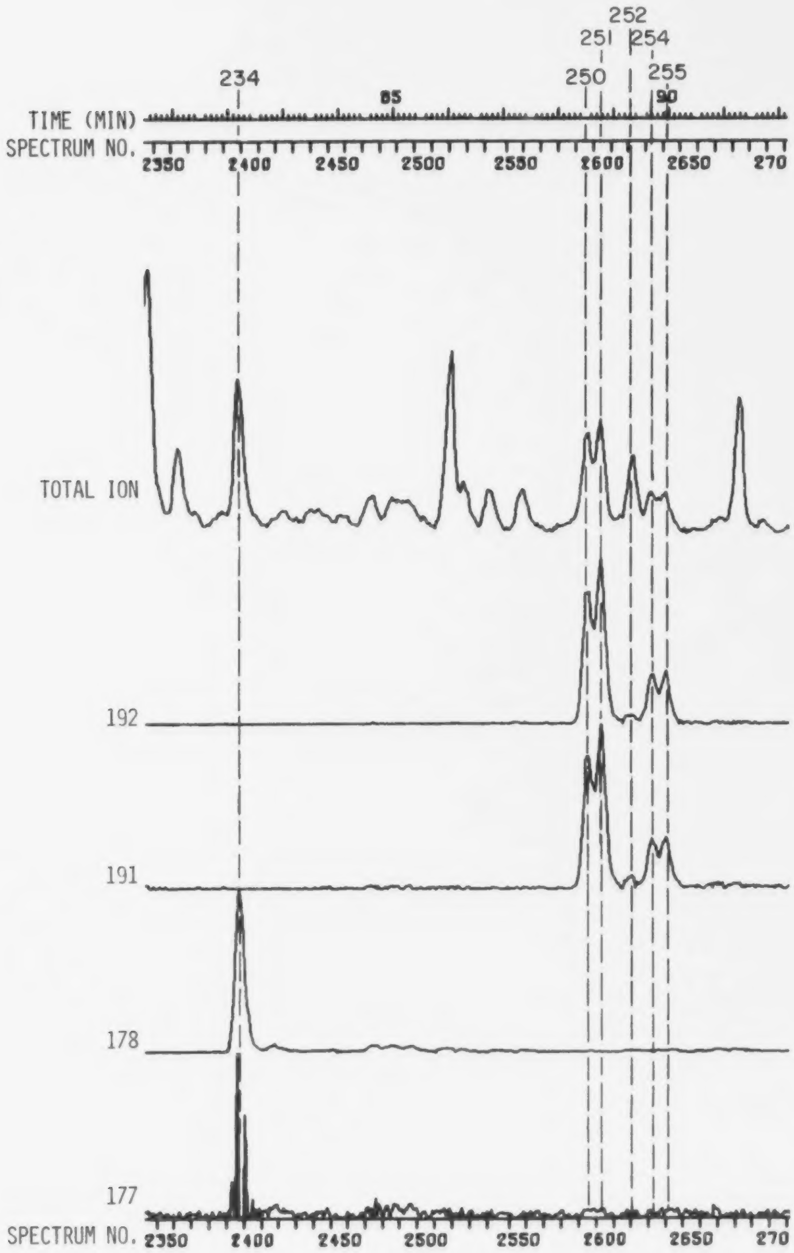


MASSGRAM PLOTS OF KEY IONS
(165, 179, 193, 194) FOR
IDENTIFYING C_2-FLUORENES



D16

MASSGRAM PLOTS OF KEY IONS (177, 178, 191, 192) FOR IDENTIFYING PHENANTHRENE, ANTHRACENE, METHYL PHENANTHRENES, AND METHYL ANTHRACENES



PHENANTHRENE/ANTHRACENE

234 Phenanthrene/Anthracene

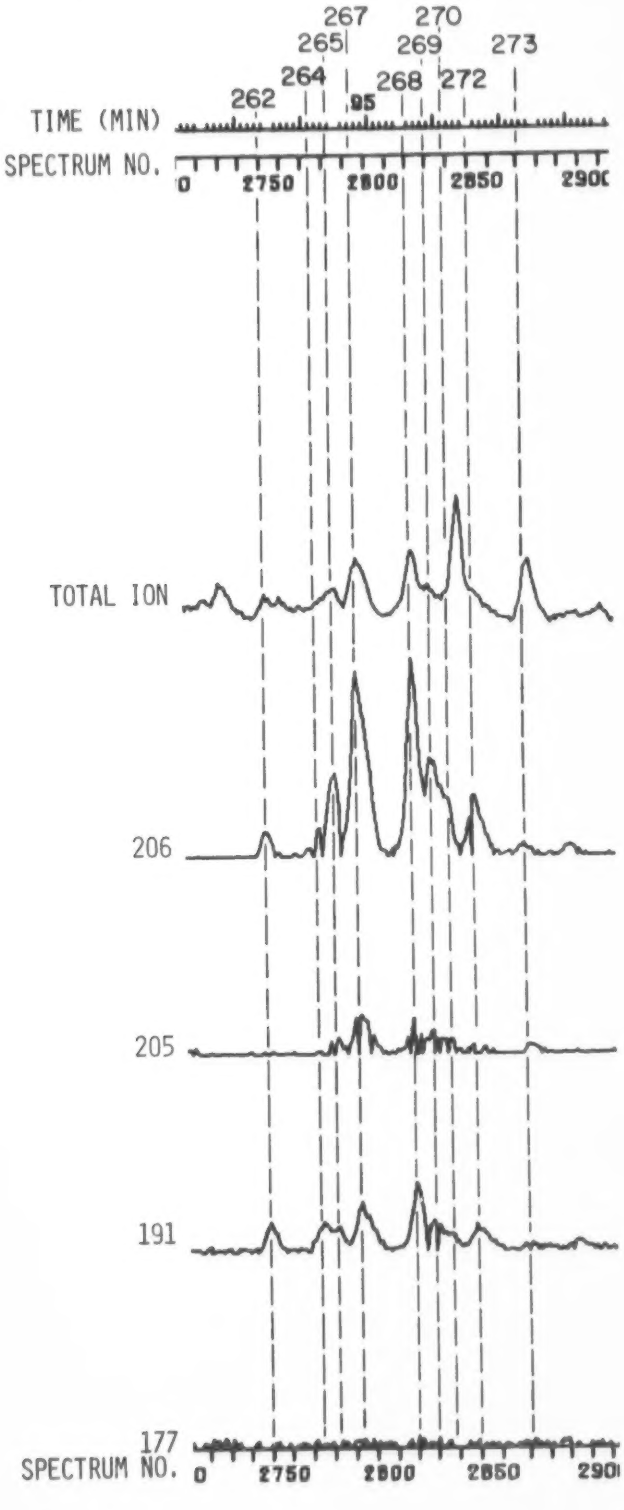
METHYL PHENANTHRENES

250 Methyl phenanthrene
251 Methyl phenanthrene
252 Methyl Phenanthrene

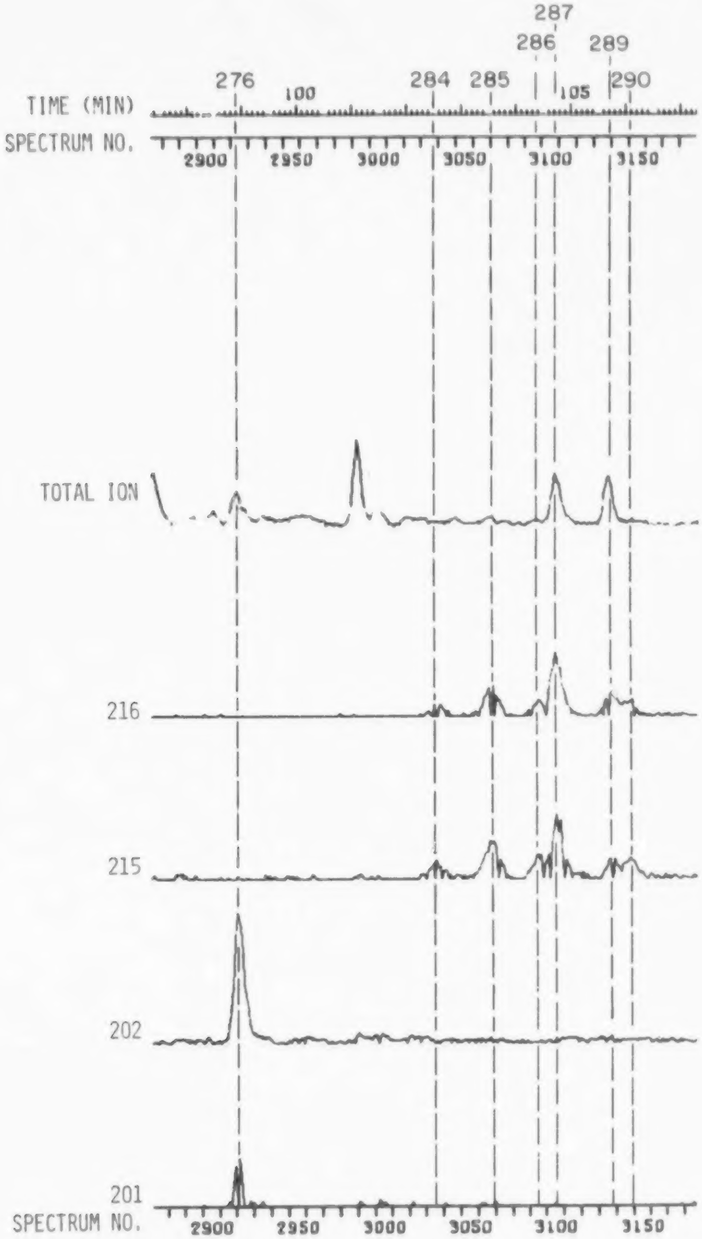
METHYL ANTHRACENES

254 2-Methyl anthracene
255 1-Methyl anthracene

MASSGRAM PLOTS OF KEY IONS (177, 191, 205, 206) FOR IDENTIFYING C_2-PHENANTHRENES AND C_2-ANTHRACENES



MASSGRAM PLOTS OF KEY IONS (201, 202, 215, 216) FOR IDENTIFYING PYRENE AND METHYL PYRENES (INCLUDES METHYL FLUORANTHENES, ACEANTHRYLENES, ACEPHENANTHRYLENES)



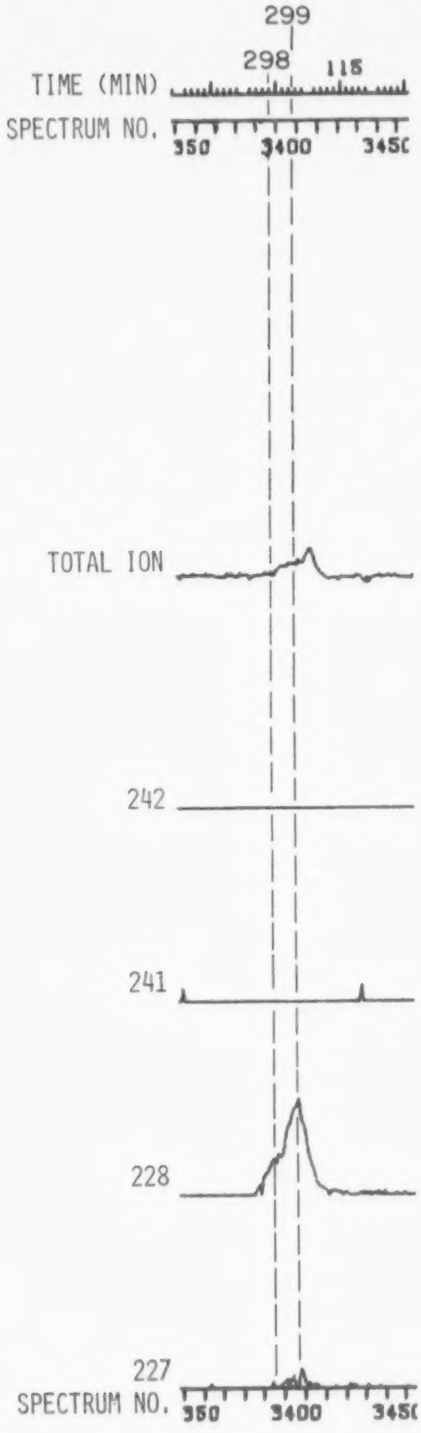
PYRENE

276

METHYL PYRENES, FLUORANTHENES, ACEANTHRYLENES, ACEPHENANTHRYLENES

284, 285, 286, 287, 289, 290

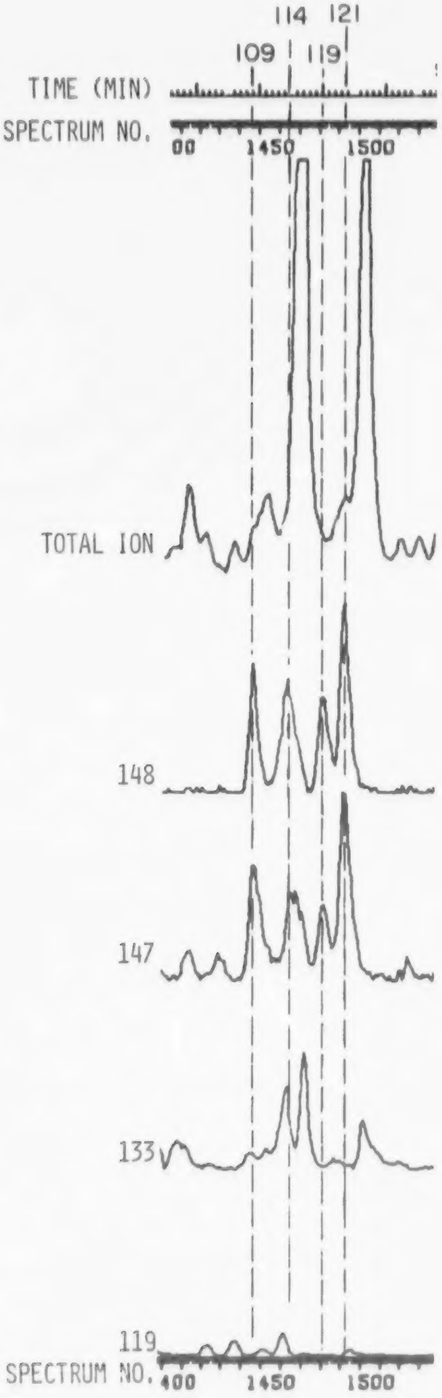
MASSGRAM PLOTS OF KEY IONS (227, 228) FOR IDENTIFYING MISCELLANEOUS PNA's



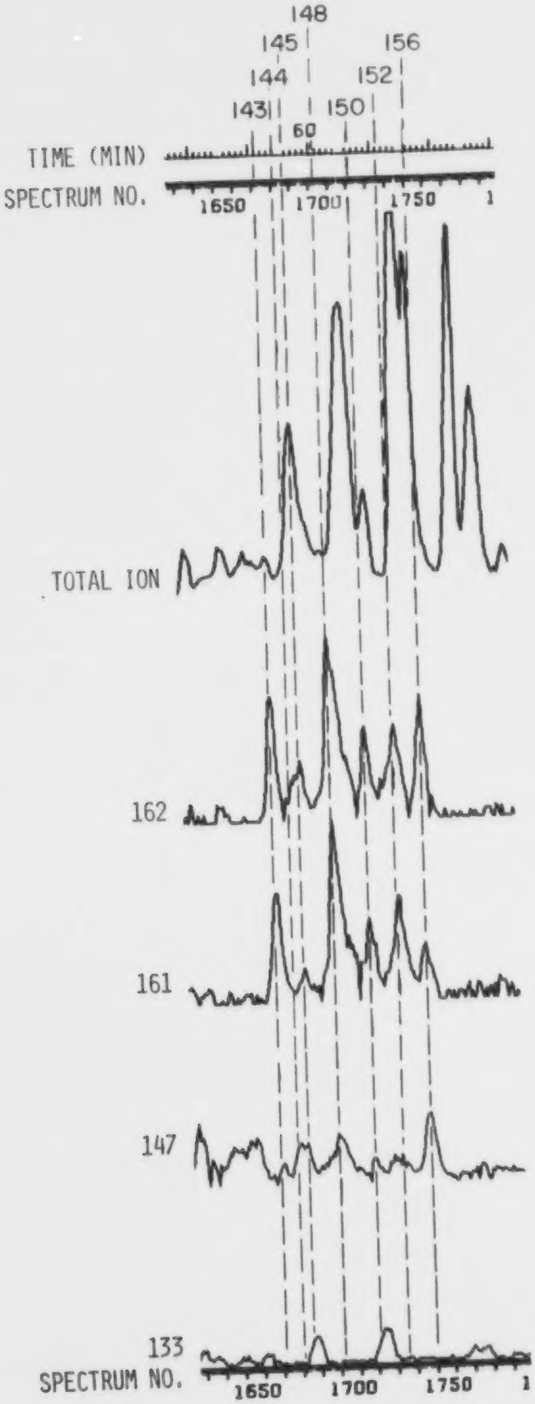
MISCELLANEOUS PNA's

298 Chrysene
299 1,2-Benzanthracene

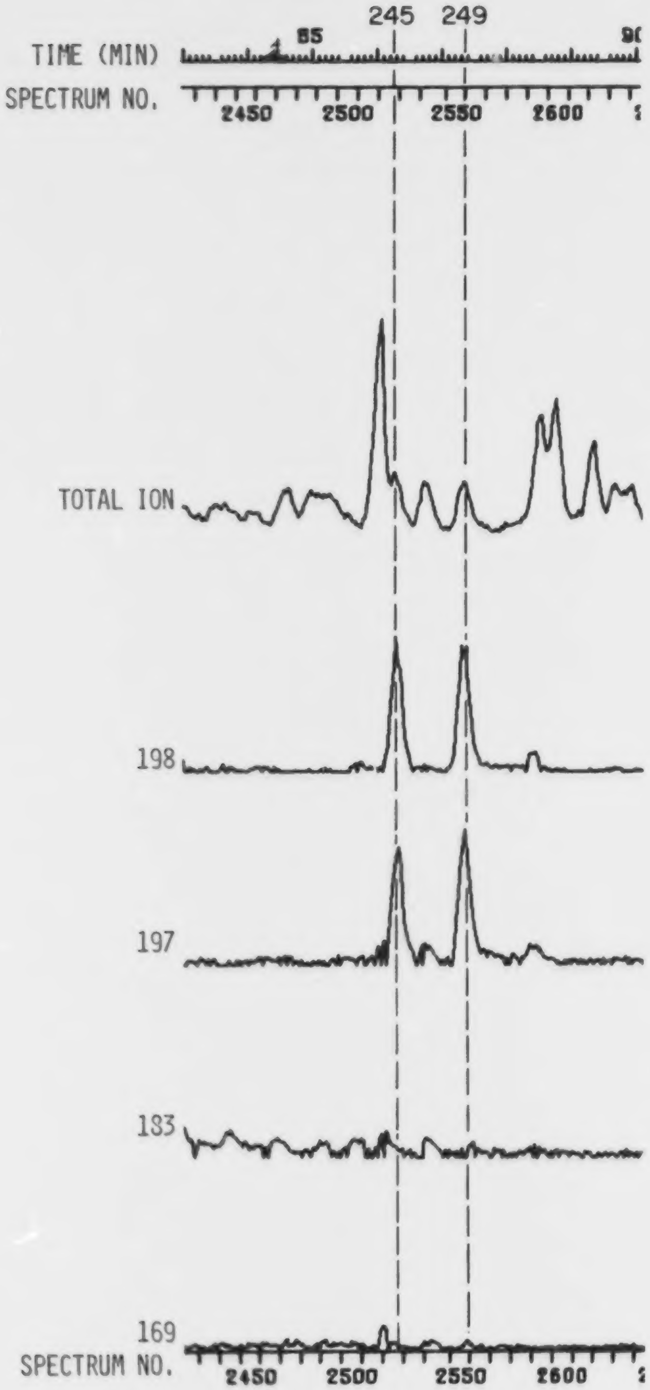
MASSGRAM PLOTS OF KEY IONS (119, 133, 147, 148) FOR IDENTIFYING METHYL BENZOTHIOPHENES



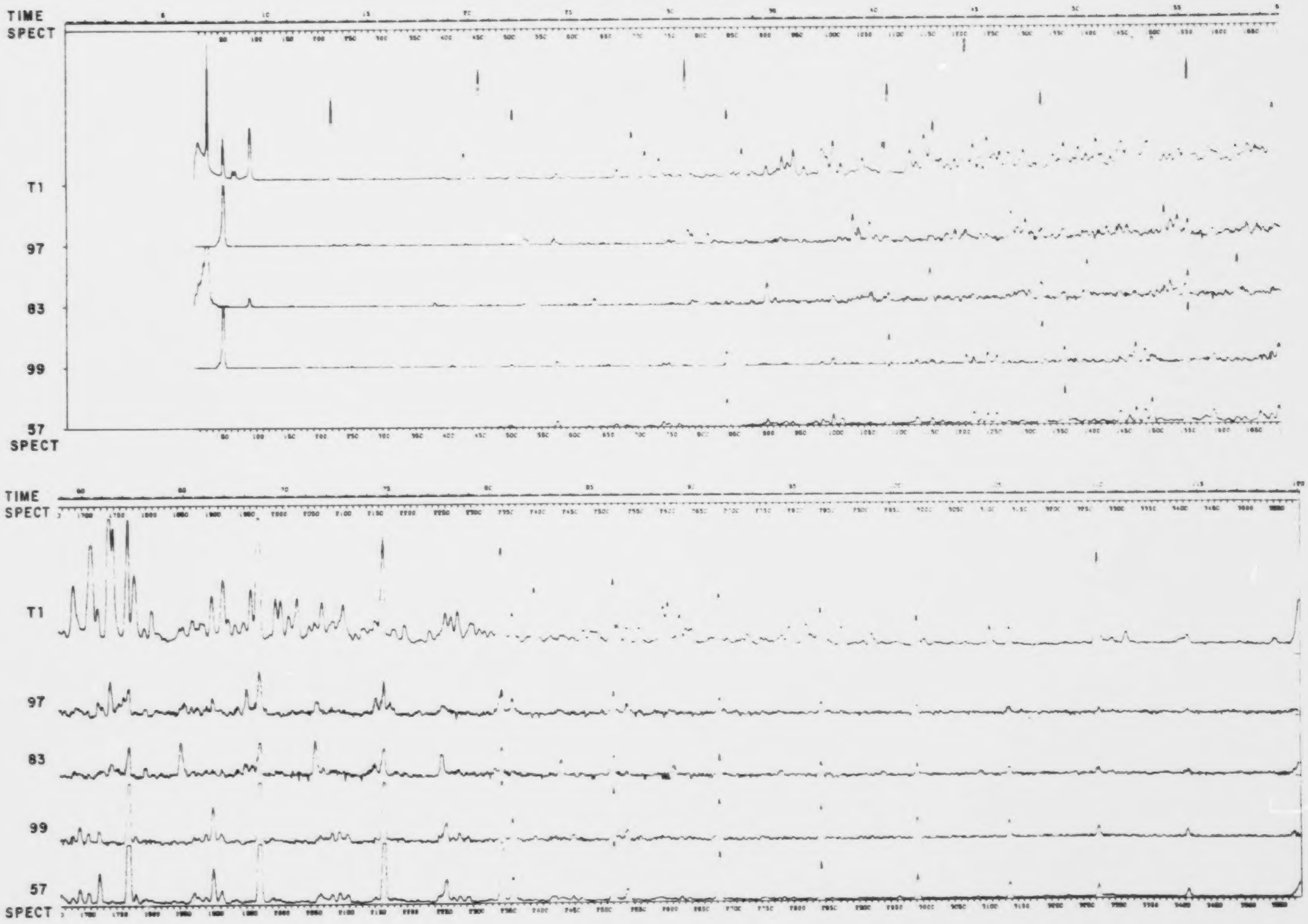
MASSGRAM PLOTS OF KEY IONS (133, 147, 161, 162) FOR IDENTIFYING C_2-BENZOTHIOPHENES



MASSGRAM PLOTS OF KEY IONS (169, 183, 197, 198) FOR IDENTIFYING METHYL DIBENZOTHIOPHENES



MASSGRAM PLOTS OF KEY IONS (57, 99) FOR IDENTIFYING ALKANES AND KEY IONS (83, 97) FOR IDENTIFYING CYCLOALKANES



APPENDIX E

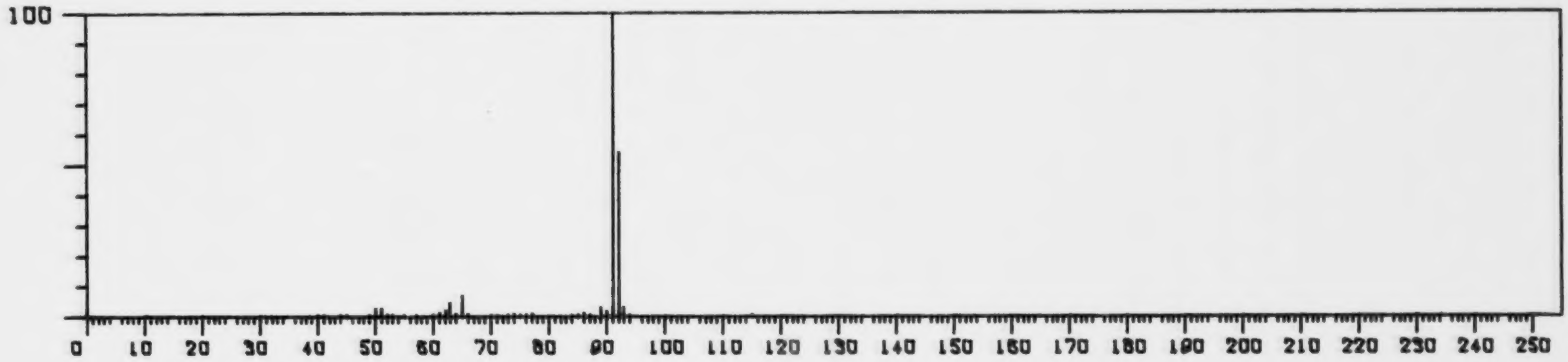
Mass Spectra for Various Compounds in the Neutral Fraction of the DAF-Effluent Sample Listed According to Increasing Retention Time

Retention Time (min.)	Compound Name	Page
13.1	toluene	E4
19.7	ethyl benzene	E5
20.4	p- and m-xylene	E6
22.1	o-xylene	E7
27.3	n-propyl benzene	E8
28.0	m-ethyl toluene	E9
28.1	p-ethyl toluene	E10
28.6	1,3,5-trimethyl benzene	E11
29.3	o-ethyl toluene	E12
32.5	n-decane & 1,2,3-trimethyl benzene (mixture)	E13
30.6	1,2,4-trimethyl benzene	E14
32.7	trimethyl benzene	E15
33.4	indan	E16
35.3	m-n-proply toluene	E17
35.6	p-n-propyl toluene & n-butyl benzene (mixture)	E18
35.9	1,3-dimethyl-5-ethyl benzene	E19
36.4	o-n-propyl toluene	E20
37.3	1,4-dimethyl-2-ethyl benzene	E21
37.4	1,3-dimethyl-4-ethyl benzene	E22
37.9	1,2-dimethyl-4-ethyl benzene	E23
40.3	1,2,4,5-tetramethyl benzene	E24
40.5	1,2,3,5-tetramethyl benzene & n-undecane (mixture)	E25
42.8	1,2,3,4-tetramethyl benzene	E26
43.1	tetralin	E27
44.4	naphthalene	E28
44.7	C_5-benzene	E29
48.2	n-dodecane	E30
50.0	dimethyl indan	E31
51.9	methyl benzothiophene	E32

Retention Time (min.)	Compound Name	Page
52.2	methyl ethyl indan	E33
52.7	2-methyl naphthalene	E34
53.0	methyl benzothiophene	E35
53.7	1-methyl naphthalene	E36
55.3	n-tridecane	E37
58.3	biphenyl	E38
59.1	dimethyl benzothiophene	E39
59.5	ethyl naphthalene	E40
60.4	dimethyl naphthalene	E41
60.7	C_{13}-alkane	E42
61.3	dimethyl naphthalene	E43
61.5	dimethyl naphthalene	E44
62.2	n-tetradecane	E45
62.5	dimethyl naphthalene	E46
63.3	dimethyl naphthalene	E47
64.9	acenaphthene	E48
65.4	methyl biphenyl	E49
66.0	methyl biphenyl	E50
68.6	n-pentadecane & some C_3-naphthalene	E51
71.1	fluorene	E52
72.3	methyl acenaphthene	E53
74.8	hexadecane	E54
75.8	C_4-naphthalene	E55
77.0	C_4-naphthalene	E56
77.8	C_4-naphthalene	E57
78.3	methyl fluorene	E58
80.5	n-heptadecane	E59
80.6	dibenzothiophene	E60
82.2	anthracene/phenanthrene	E61
84.6	C_2-fluorene	E62
84.9	C_2-fluorene	E63
85.2	C_2-fluorene	E64

Retention Time (min.)	Compound Name	Page
86.0	n-octadecane	E65
86.2	methyl dibenzothiophene	E66
87.3	methyl dibenzothiophene	E67
88.5	methyl phenanthrene	E68
88.7	methyl phenanthrene	E69
89.6	2-methyl anthracene	E70
89.9	1-methyl anthracene	E71
91.2	n-nonadecane	E72
98.9	pyrene	E73
101.1	n-heneicosane	E74
105.6	n-docosane	E75
113.9	chrysene	E76
114.2	1,2-benzathracene	E77

FRN 13201 SPEC 220 RET. TIME 13. 1 TOLUENE

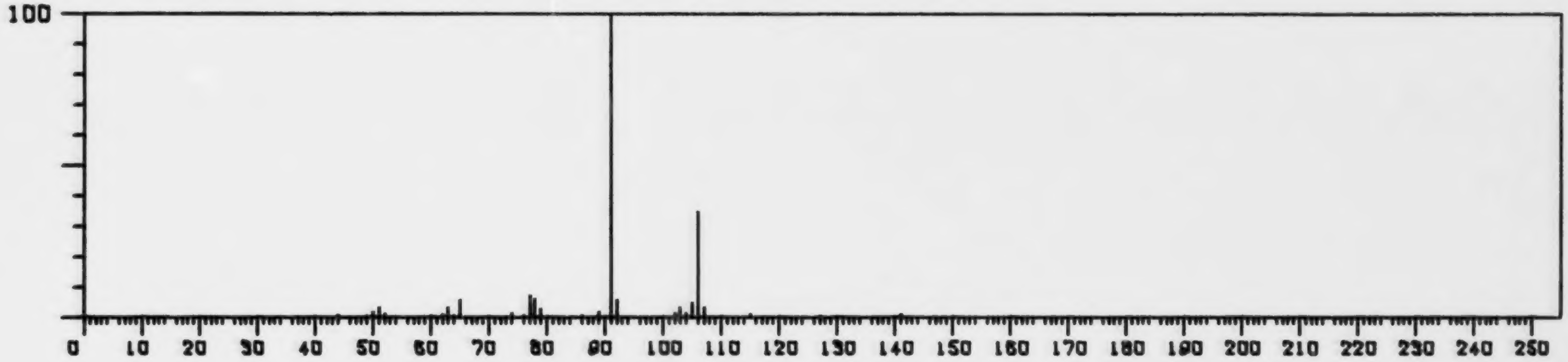


E4

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

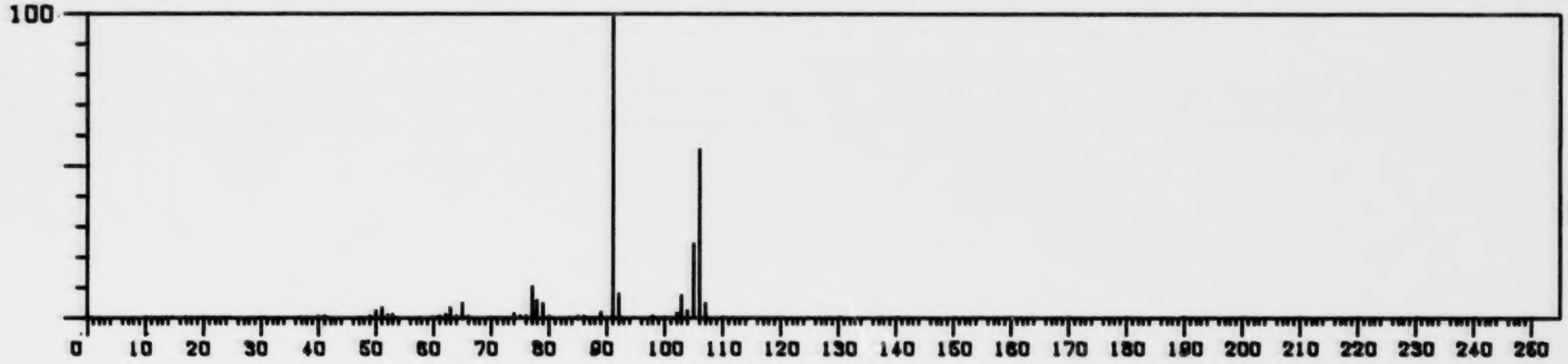
FRN 13201 SPEC 428 RET. TIME 18. 7 ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

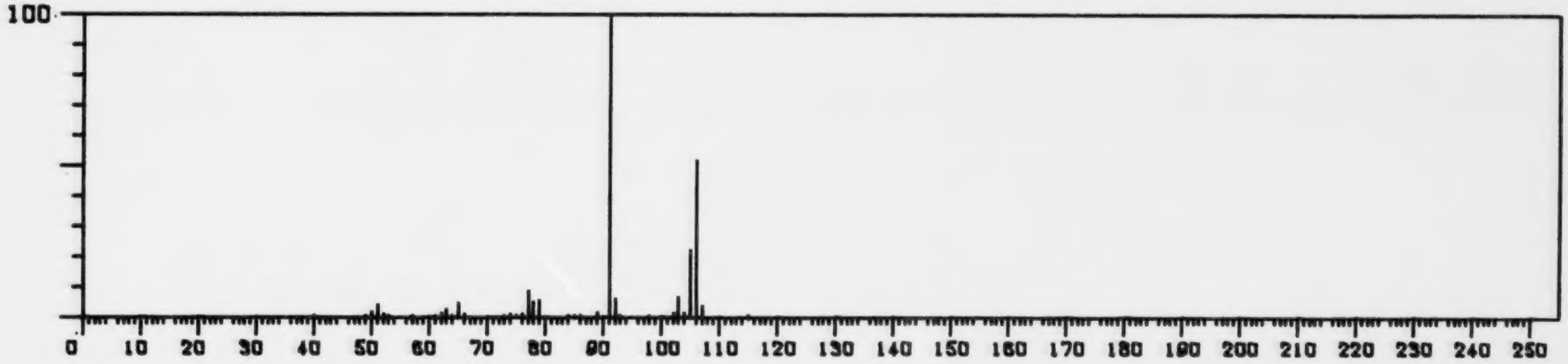
FRN 13201 SPEC 452 RET. TIME 20. 4 P & M-XYLENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 505 RET. TIME 22. 1 O-XYLENE

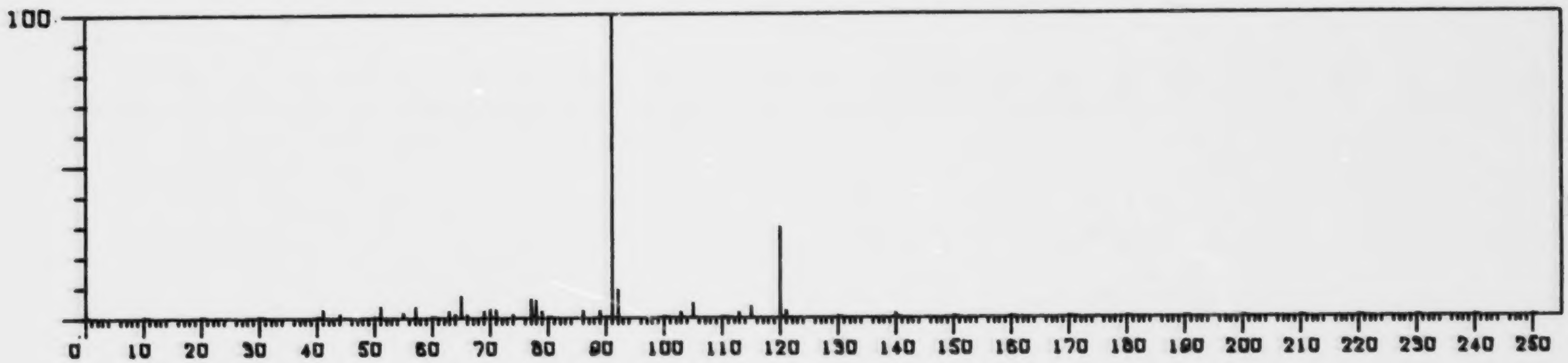


E7

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

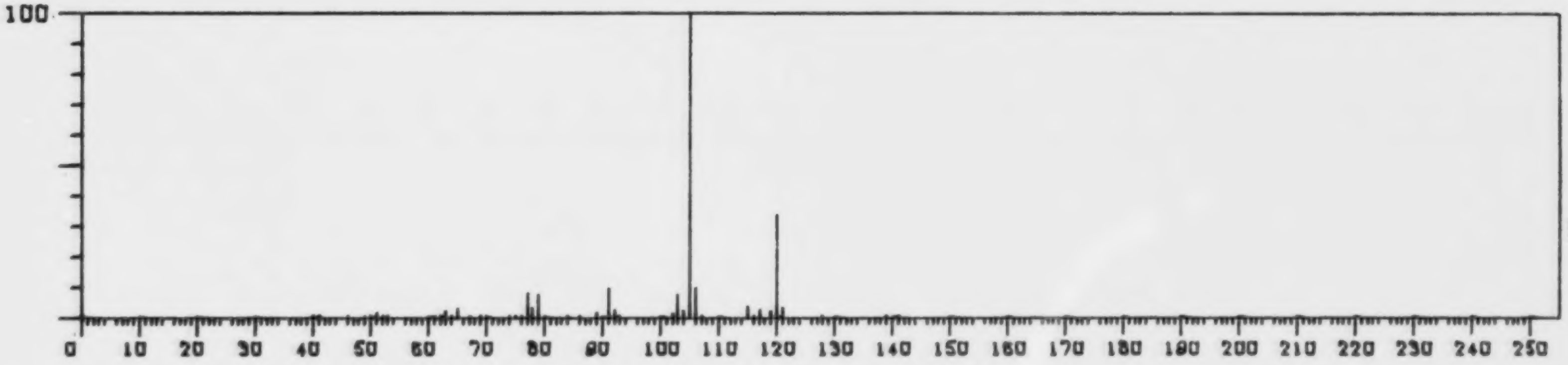
FRN 13201 SPEC 668 RET. TIME 27. 3 N-PROPYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

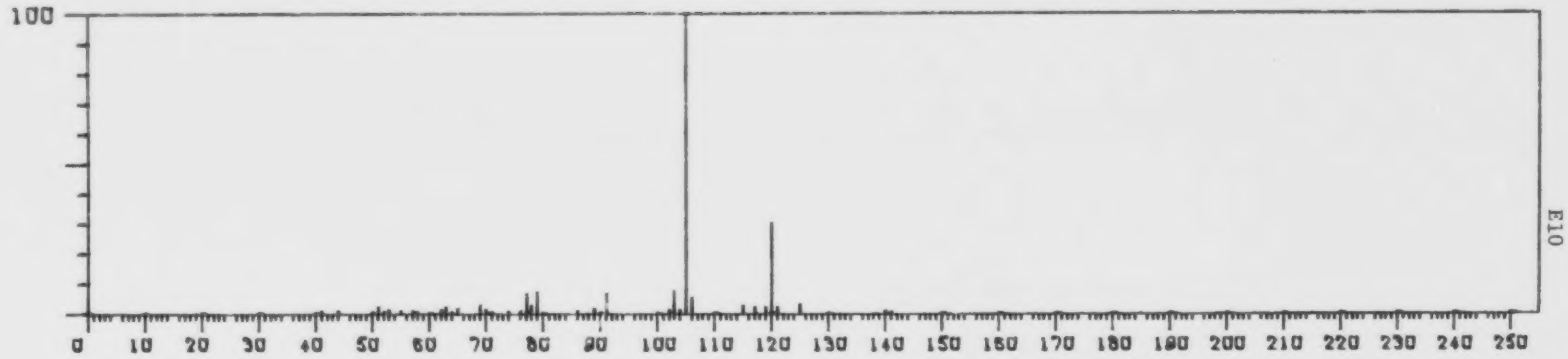
FRN 13201 SPEC 691 RET. TIME 28. 0 M-ETHYL TOLUENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

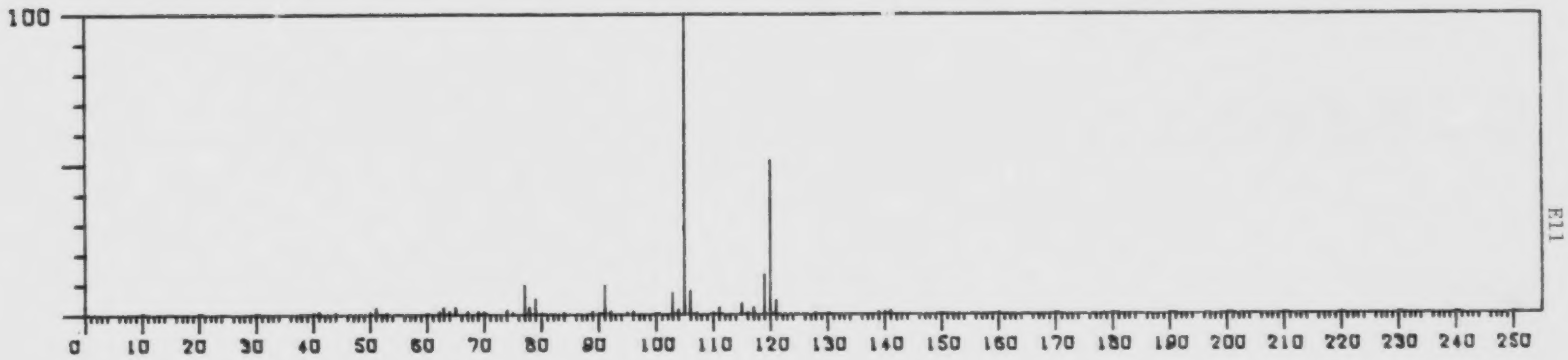
FRN 13201 SPEC 686 RET. TIME 28. 1 P-ETHYL TOLUENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

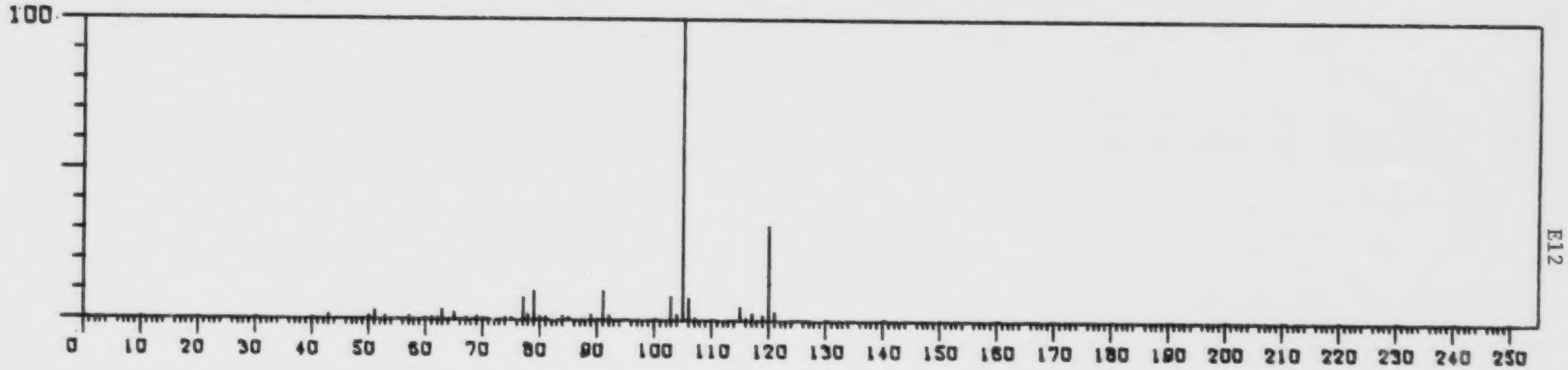
FRN 13201 SPEC 712 RET. TIME 28. 6 1.3.5-TRIMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 734 RET. TIME 28. 3 0-ETHYL TOLUENE

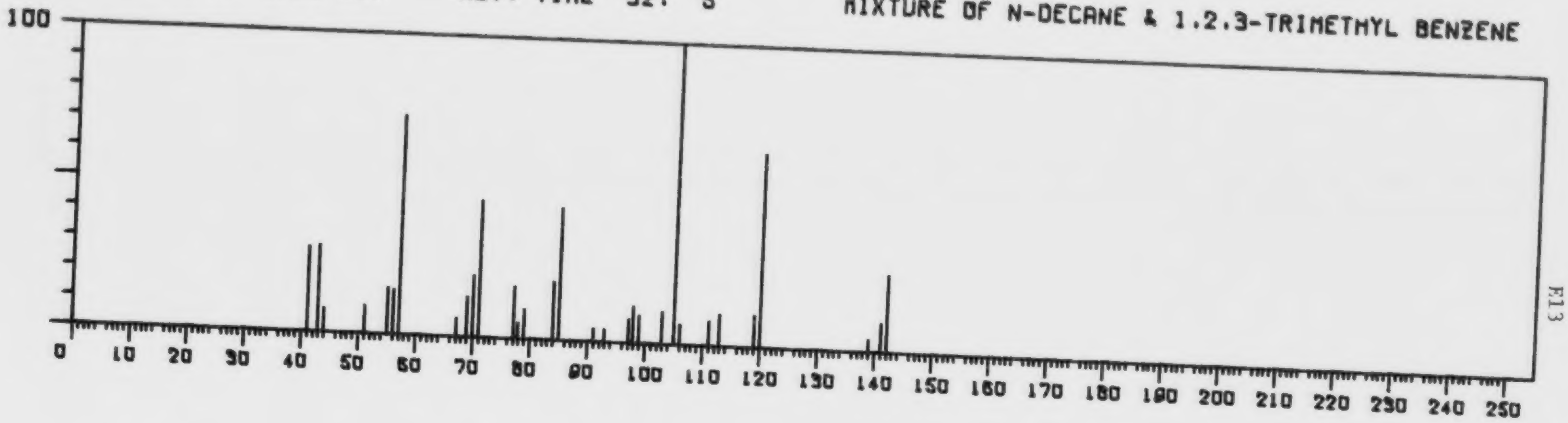


E12

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

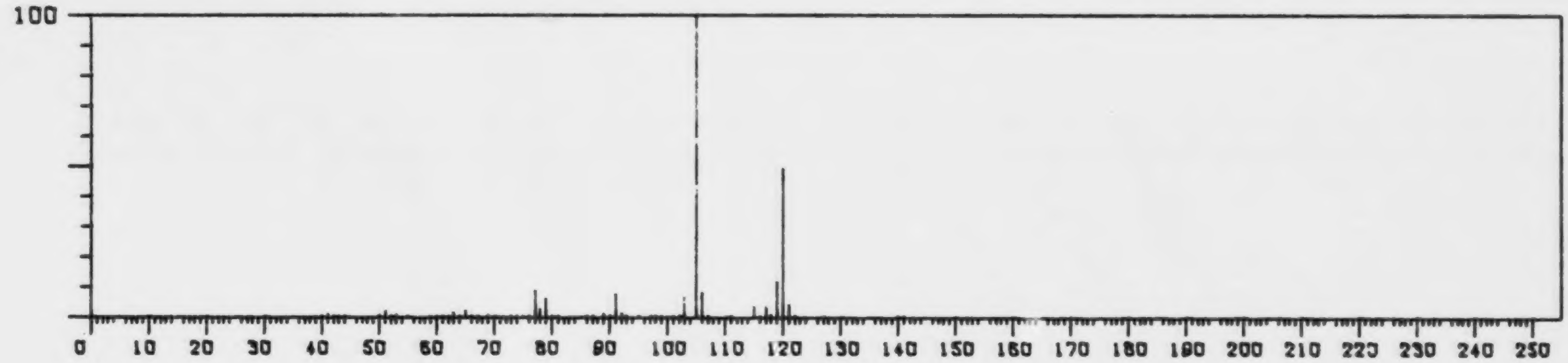
FRN 13201 SPEC 837 RET. TIME 32. 5 MIXTURE OF N-DECANE & 1.2.3-TRIMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

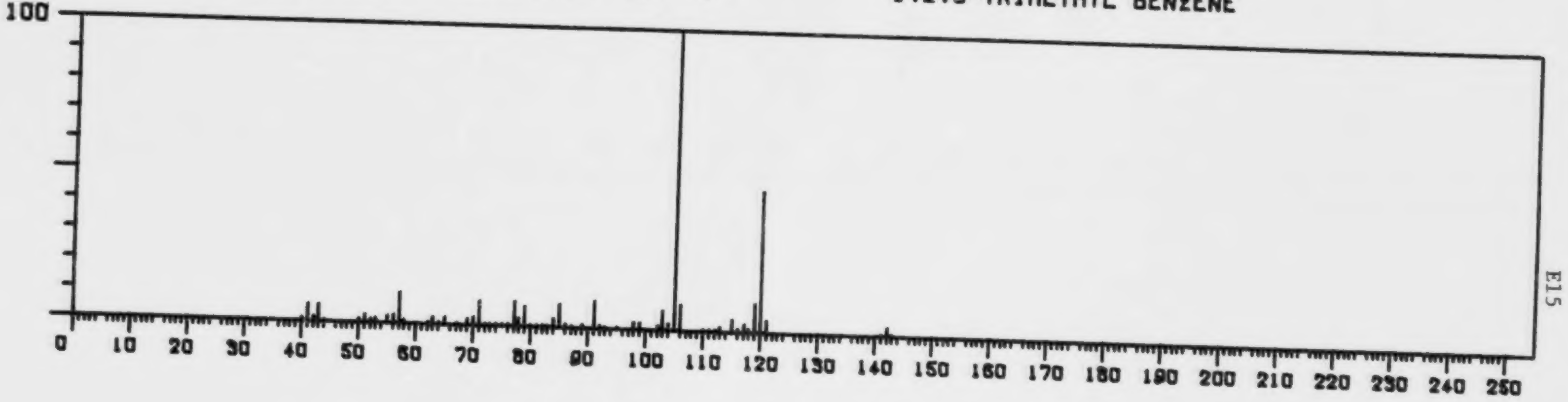
FRN 13201 SPEC 776 RET. TIME 30. 6 1.2.4-TRIMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

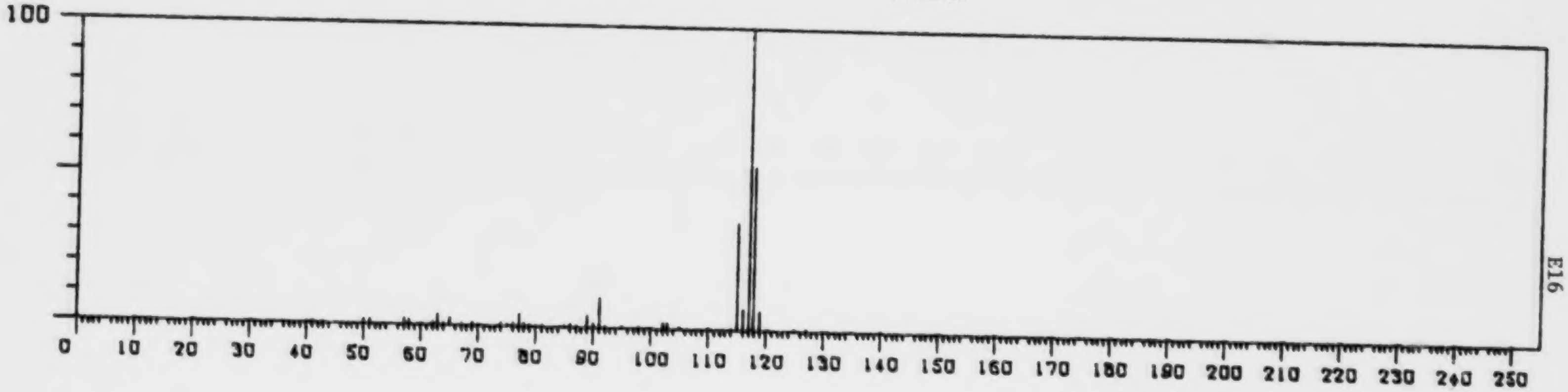
FRN 13201 SPEC 842 RET. TIME 32. 7 1.2.3-TRIMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

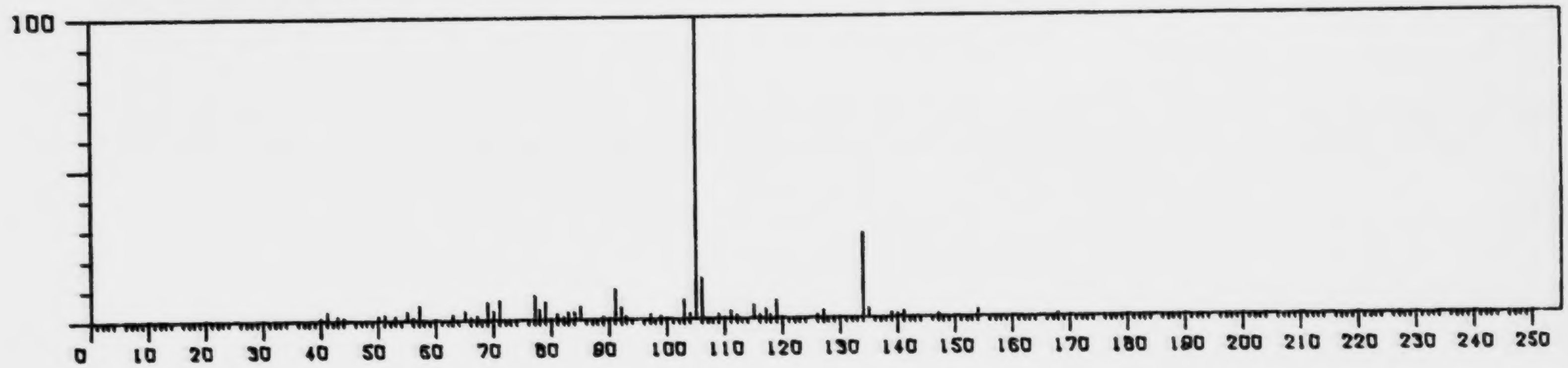
FRN 13201   SPEC 865   RET. TIME 33. 4   INDAN



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

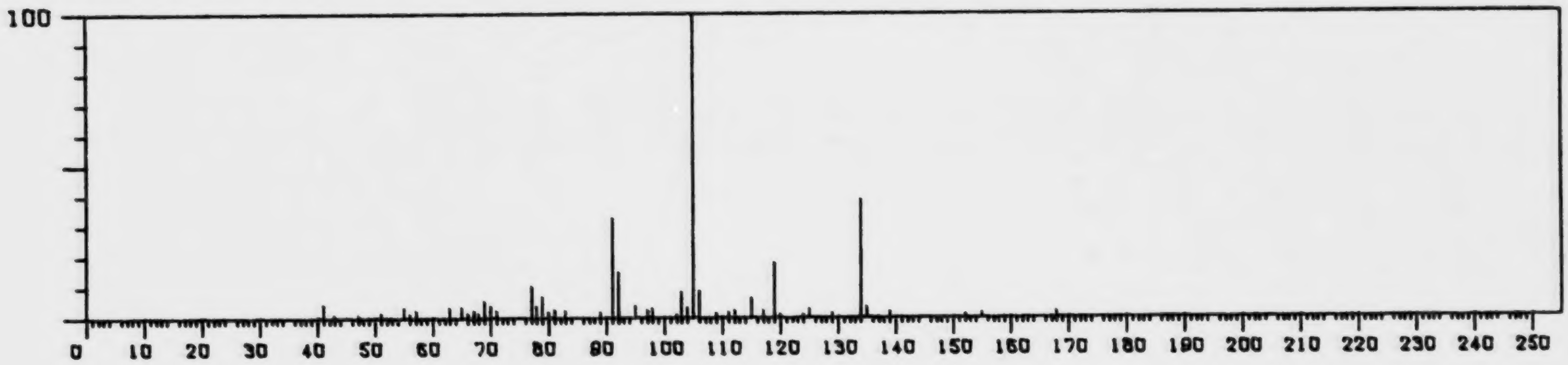
FRN 13201 SPEC 927 RET. TIME 35. 3 M-N-PROPYL TOLUENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

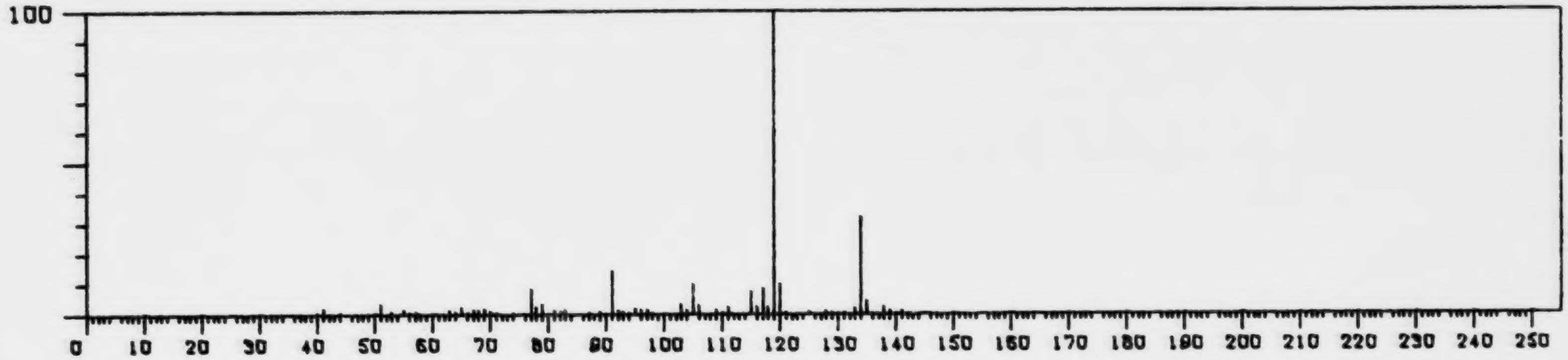
FRN 13201 SPEC 935 RET. TIME 35. 6 MIXTURE OF P-N-PROPYL TOLUENE & N-BUTYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

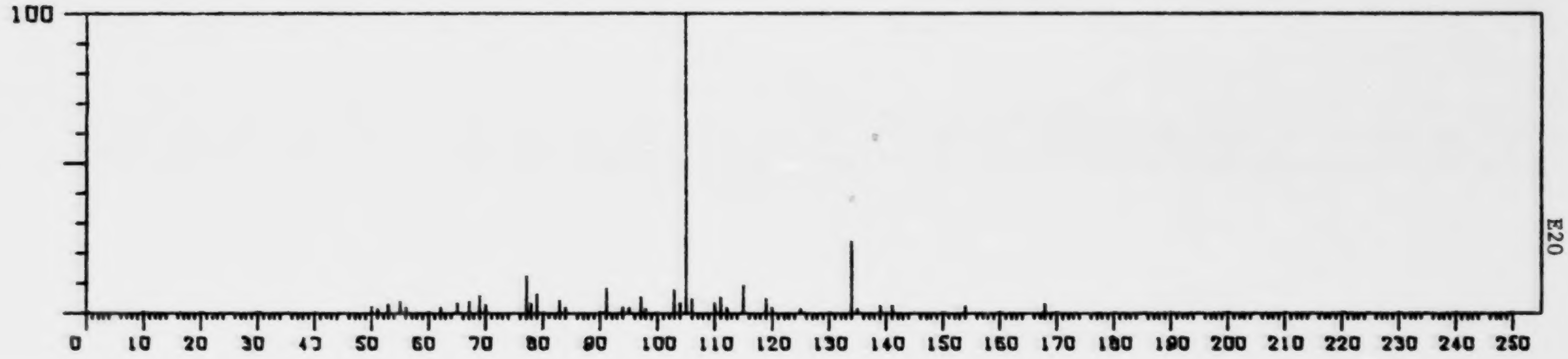
FRN 13201   SPEC 945   RET. TIME 35. 9   1.3-DIMETHYL-5-ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

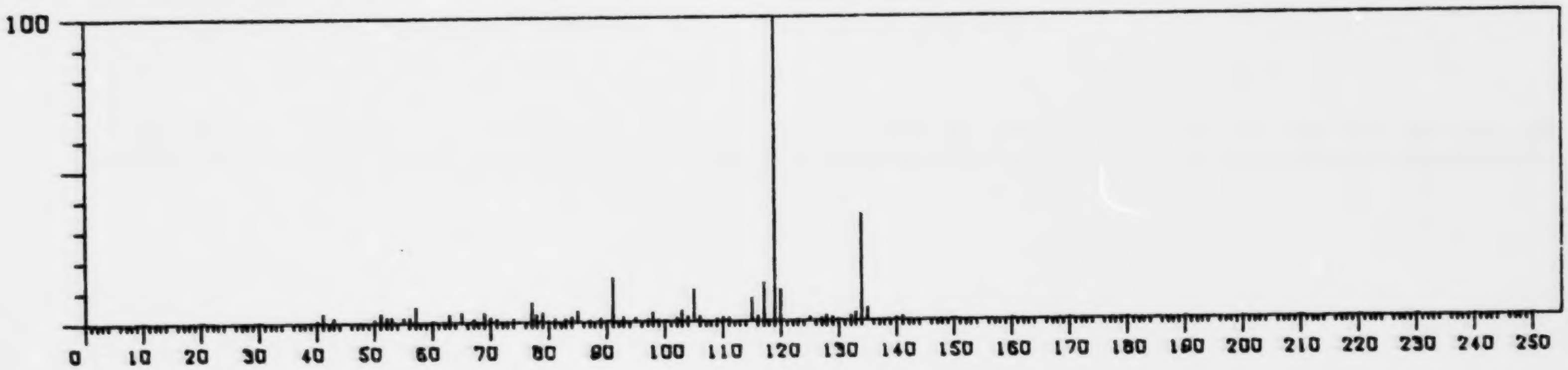
FRN 13201 SPEC 959 RET. TIME 36. 4 O-N-PROPYL TOULENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

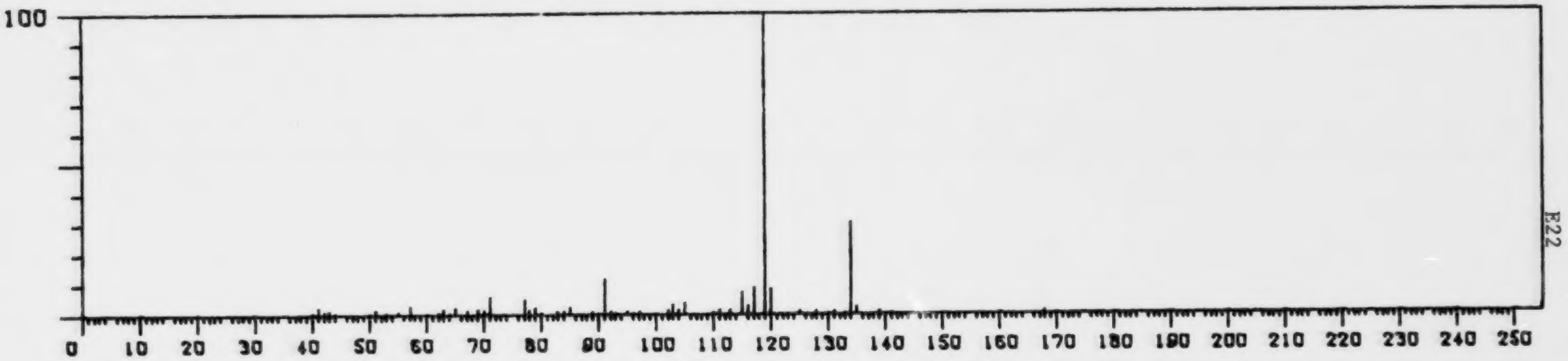
FRN 13201 SPEC 987 RET. TIME 37. 3 1.4-DIMETHYL-2-ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

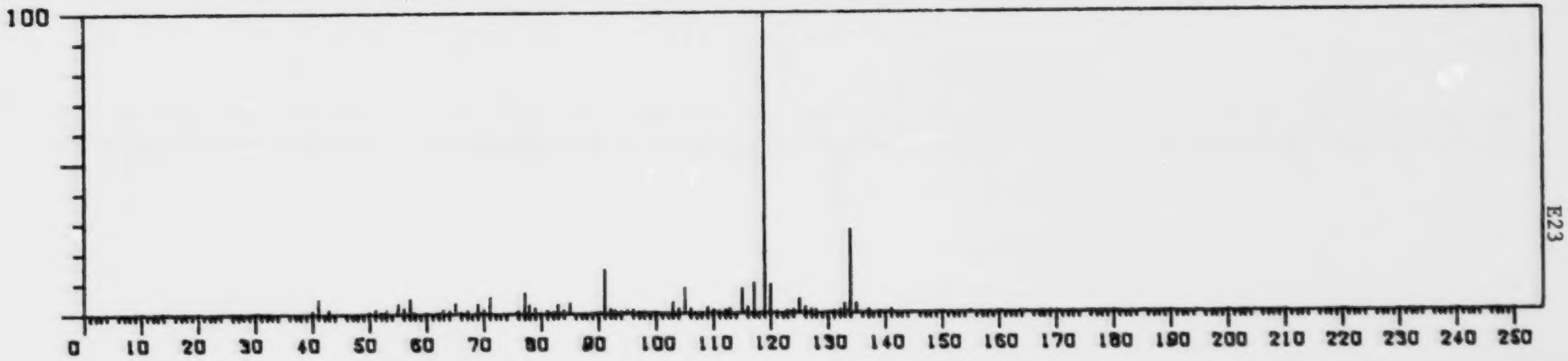
FRN 13201 SPEC 990 RET. TIME 37. 4 1.3-DIMETHYL-4-ETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1005 RET. TIME 37. 9 1.2-DIMETHYL-4-ETHYL BENZENE

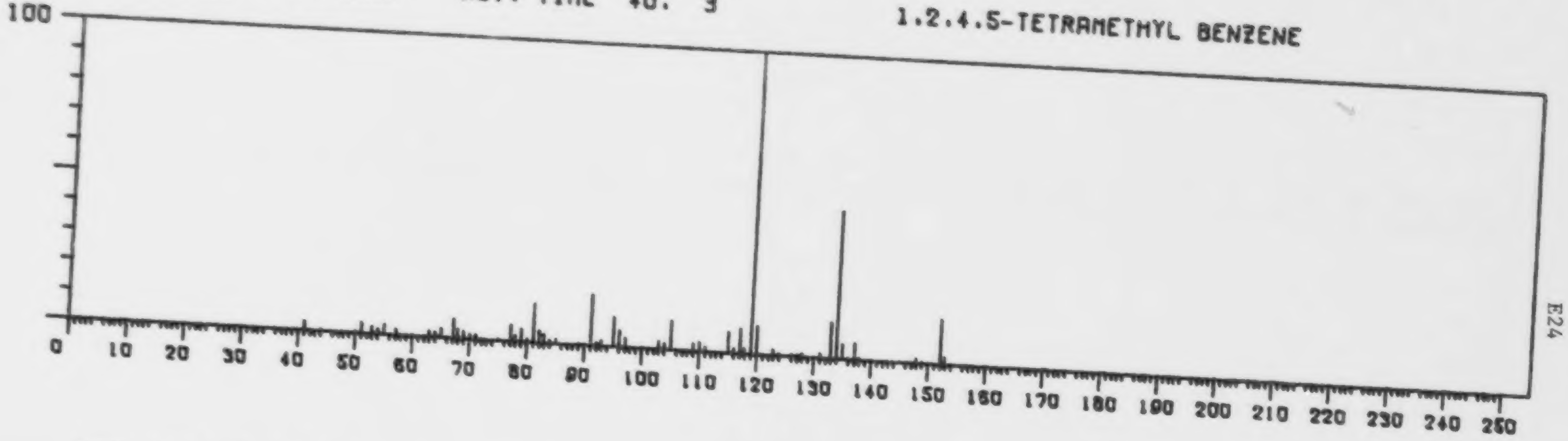


E23

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

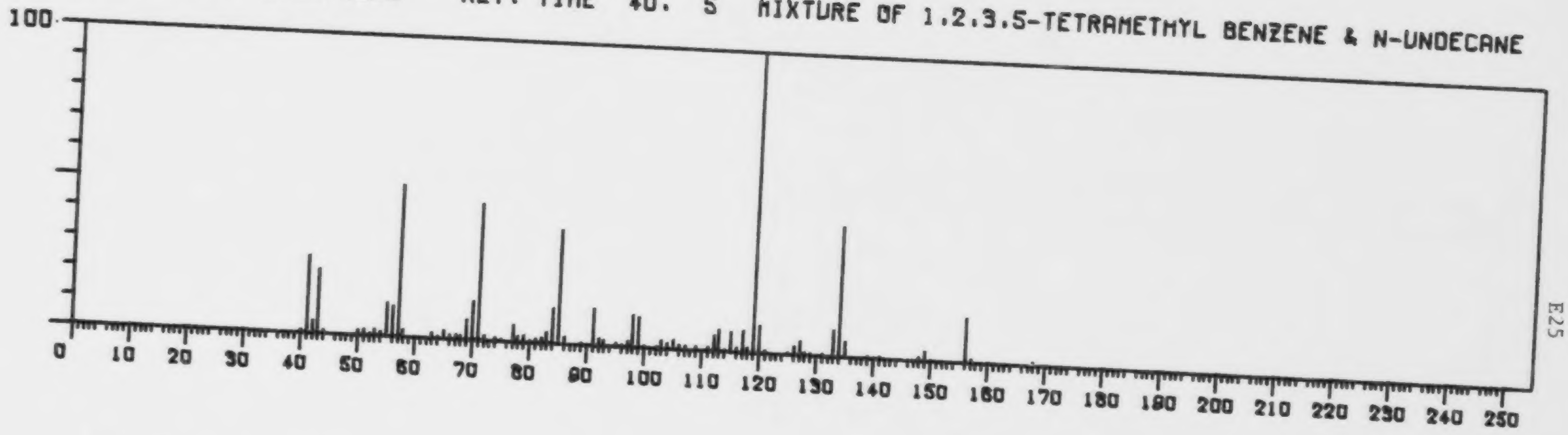
FRN 13201 SPEC 1082 RET. TIME 40. 3 1.2.4.5-TETRAMETHYL BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

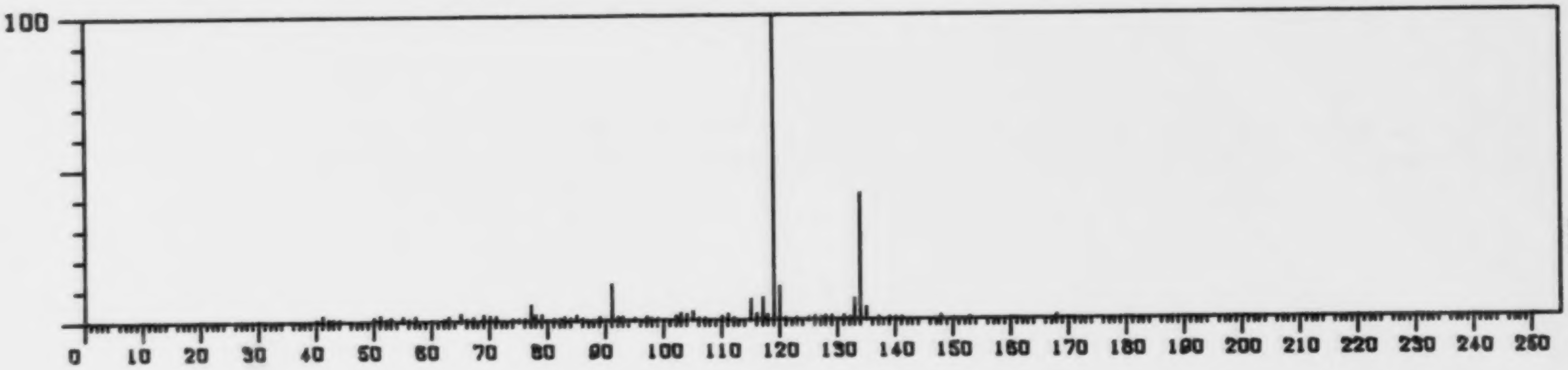
FRN 13201   SPEC 1080   RET. TIME 40. 5   MIXTURE OF 1.2.3.5-TETRAMETHYL BENZENE & N-UNDECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1162 RET. TIME 42. 8 1.2.3.4-TETRAMETHYL BENZENE

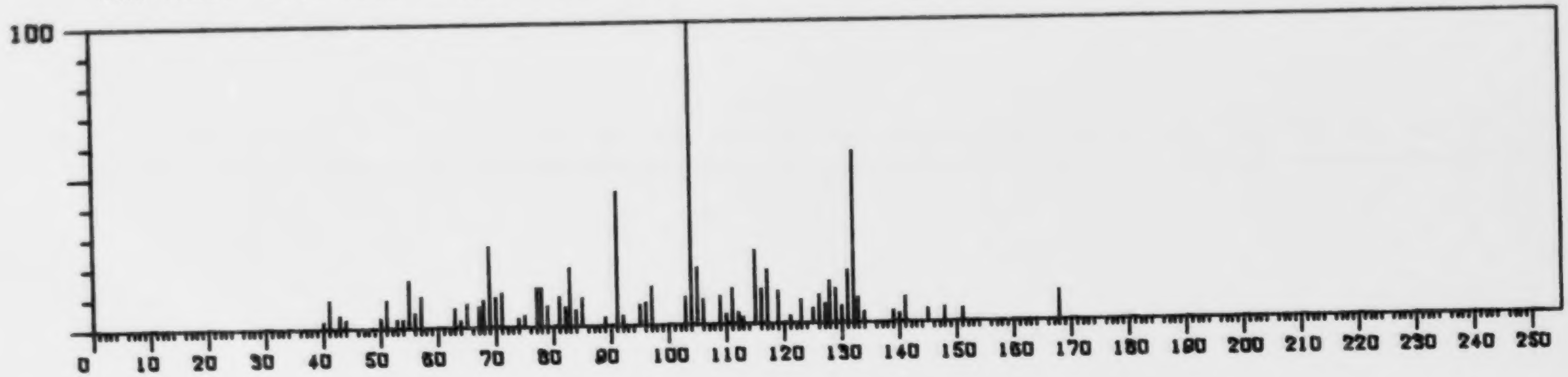


E26

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

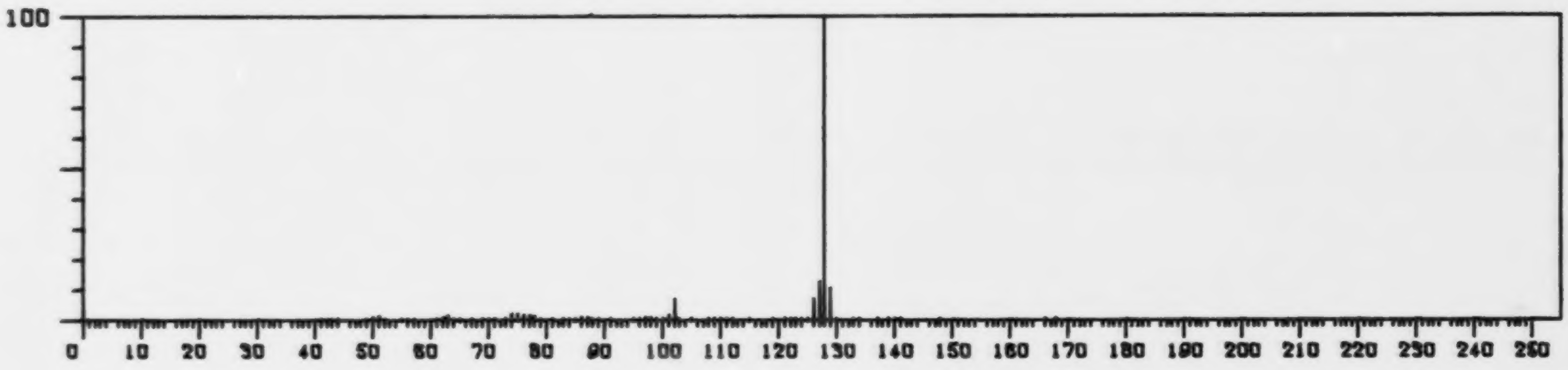
FRN 13201 SPEC 1170 RET. TIME 43. 1 TETRALIN



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

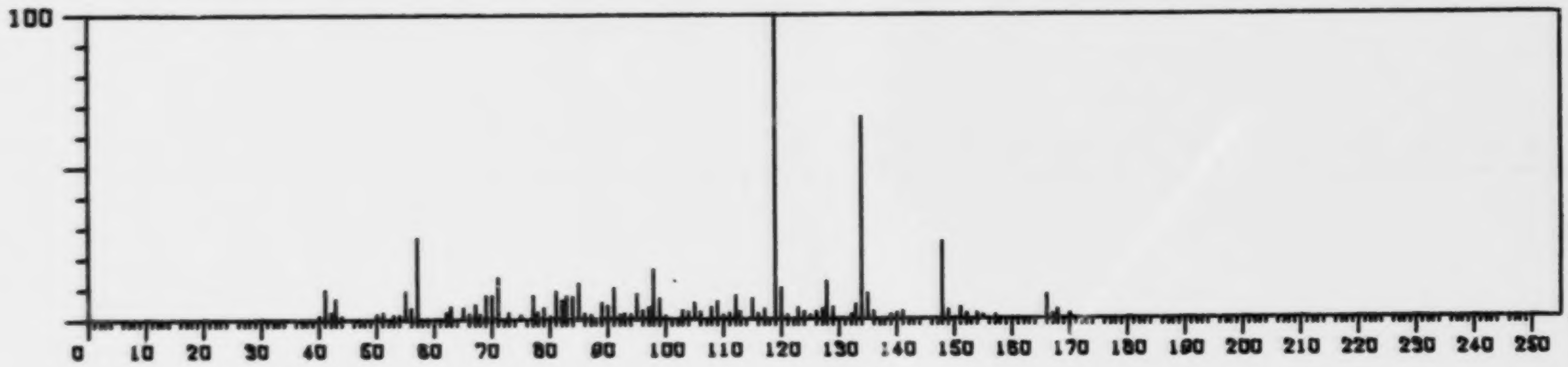
FRN 13201 SPEC 1213   RET. TIME 44. 4   NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

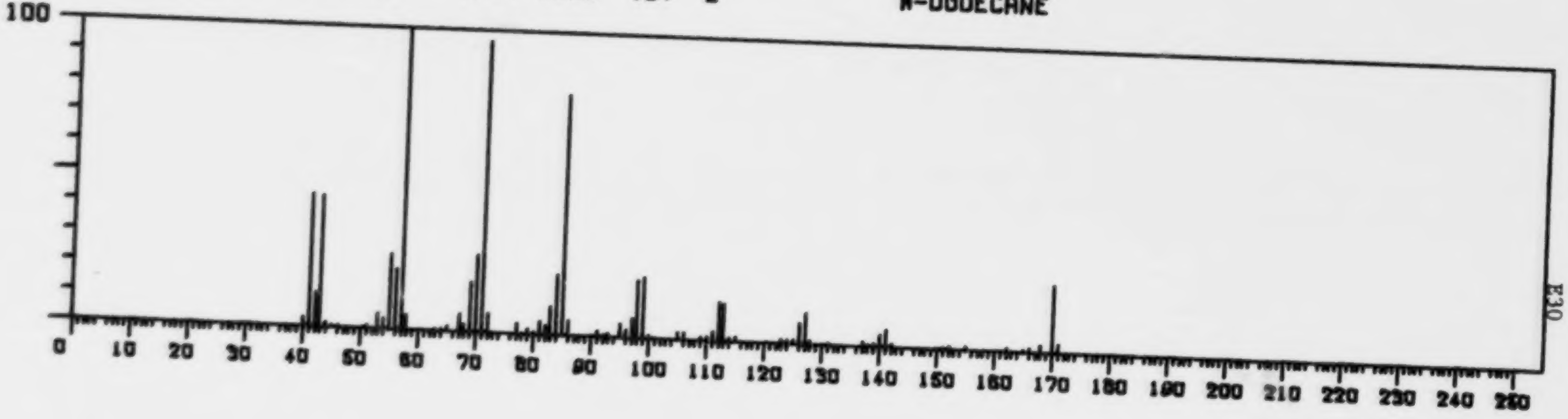
FRN 13201 SPEC 1224   RET. TIME 44. 7   C5-BENZENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

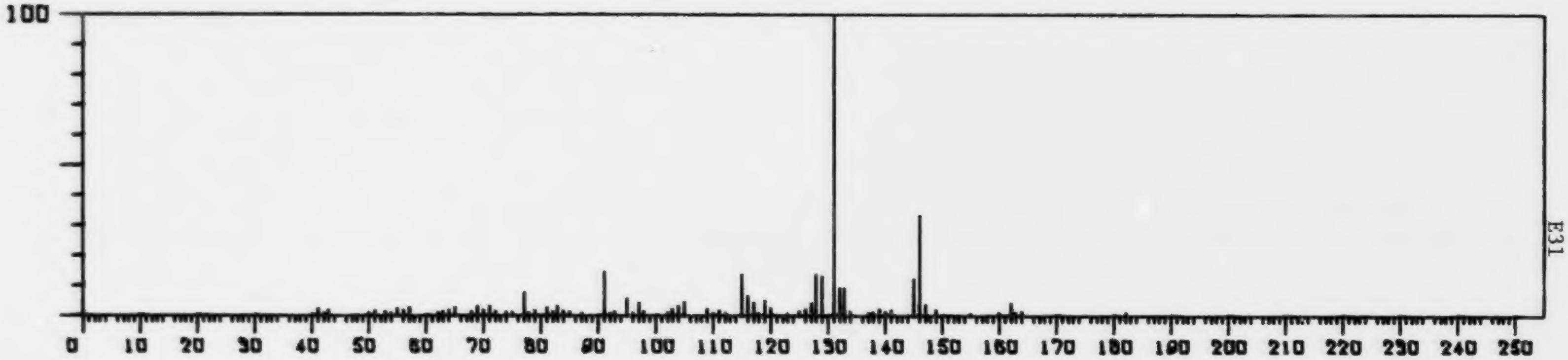
FRN 13201 SPEC 1329 RET. TIME 48. 2 N-DODECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201   SPEC 1387   RET. TIME 50. 0   DIMETHYL INDAN

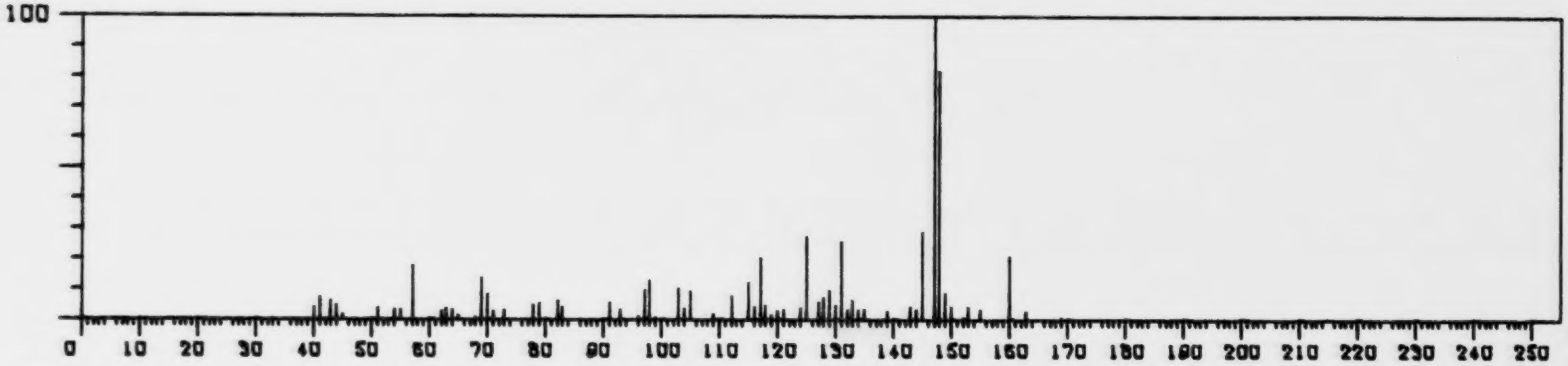


E31

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1447-1442 RET. TIME 51. 8 METHYL BENZOTHIOPHENE

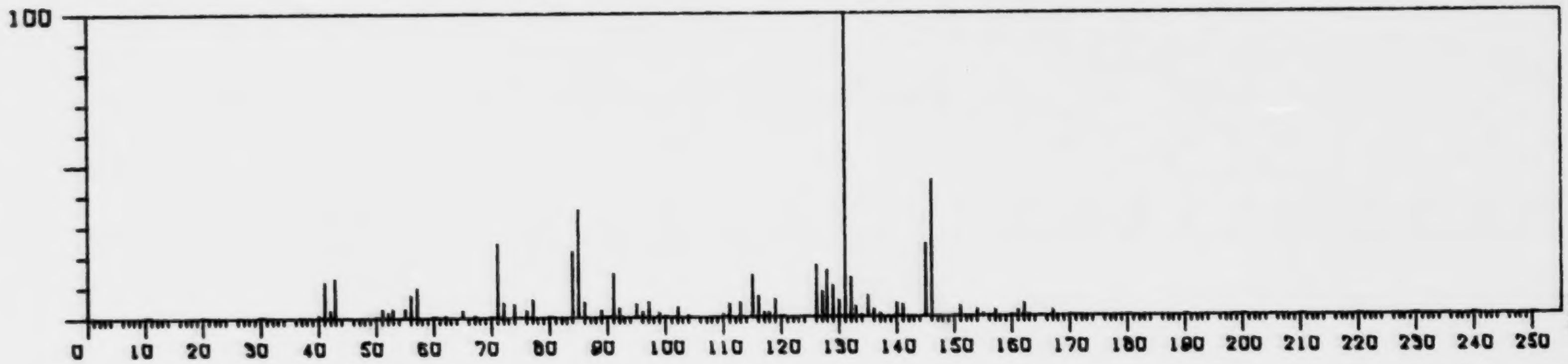


AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 1454-1447 RET. TIME 52. 2 METHYL ETHYL INDAN

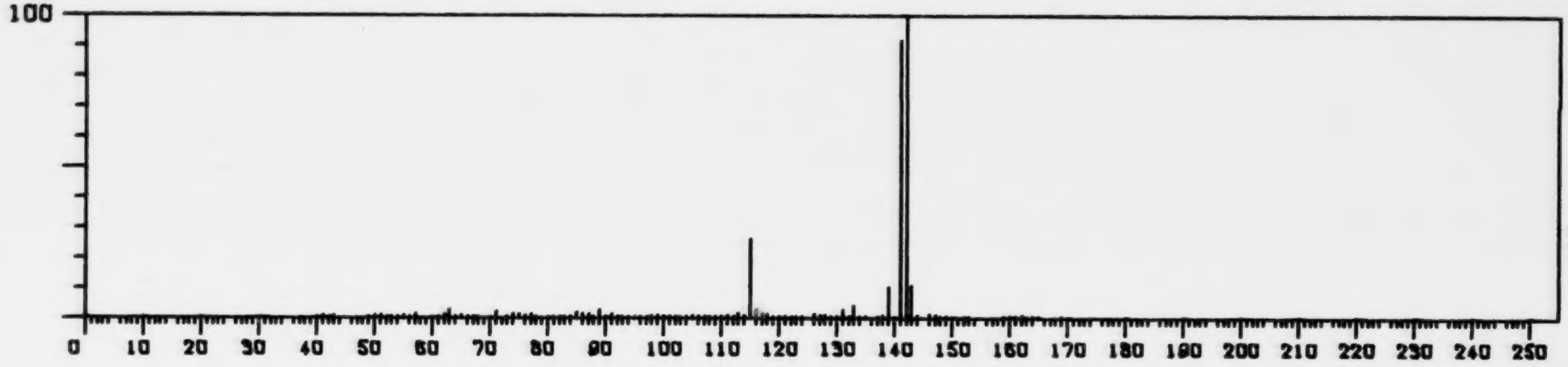


AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

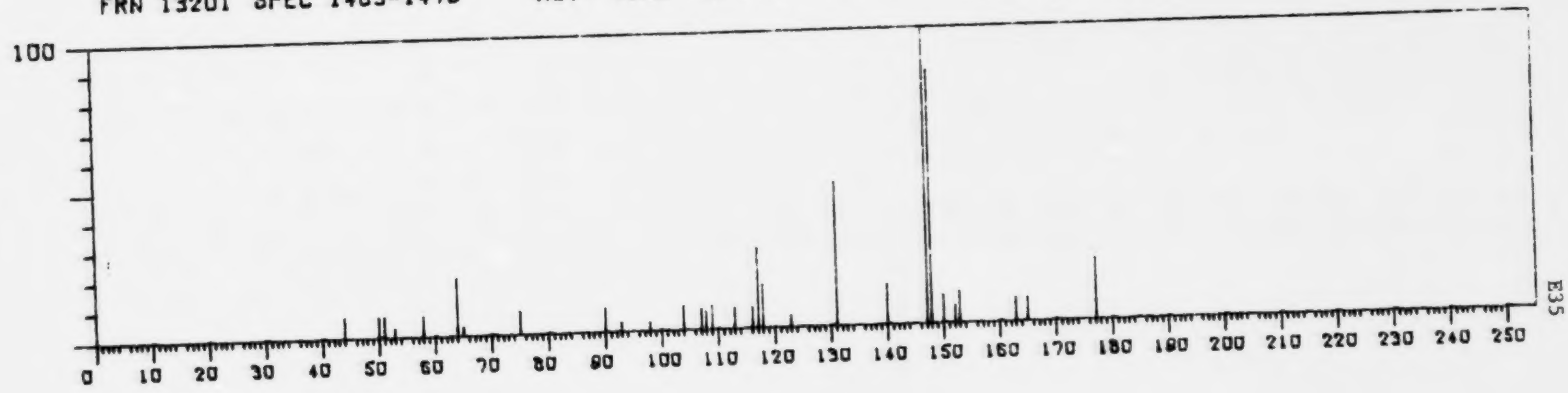
FRN 13201 SPEC 1473 RET. TIME 52. 7 2-METHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1483-1479 RET. TIME 53. 0 METHYL BENZOTHIOPHENE

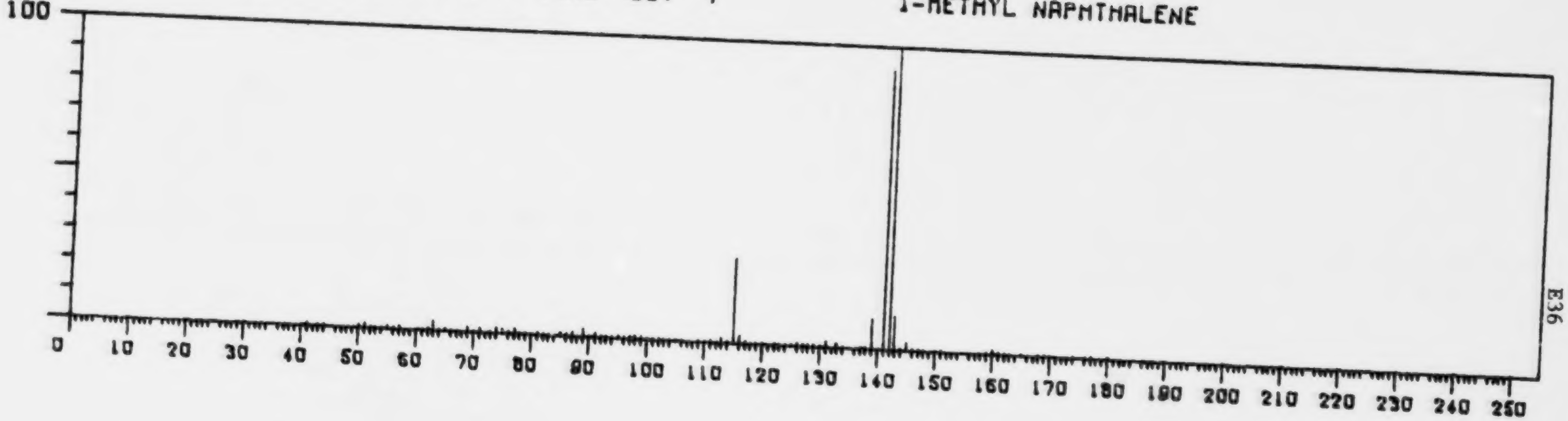


AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.OIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

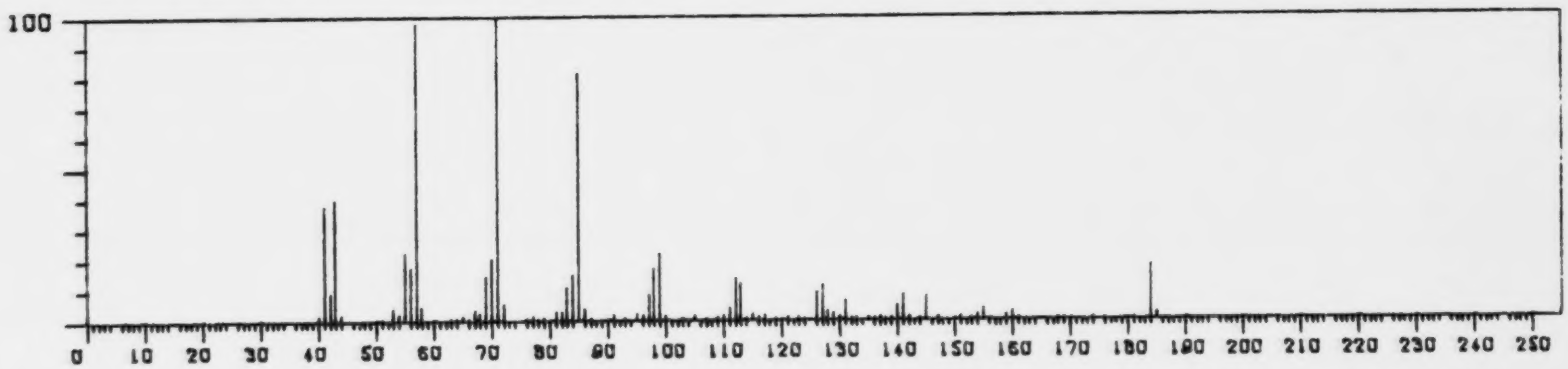
FRN 13201 SPEC 1505 RET. TIME 53. 7 1-METHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

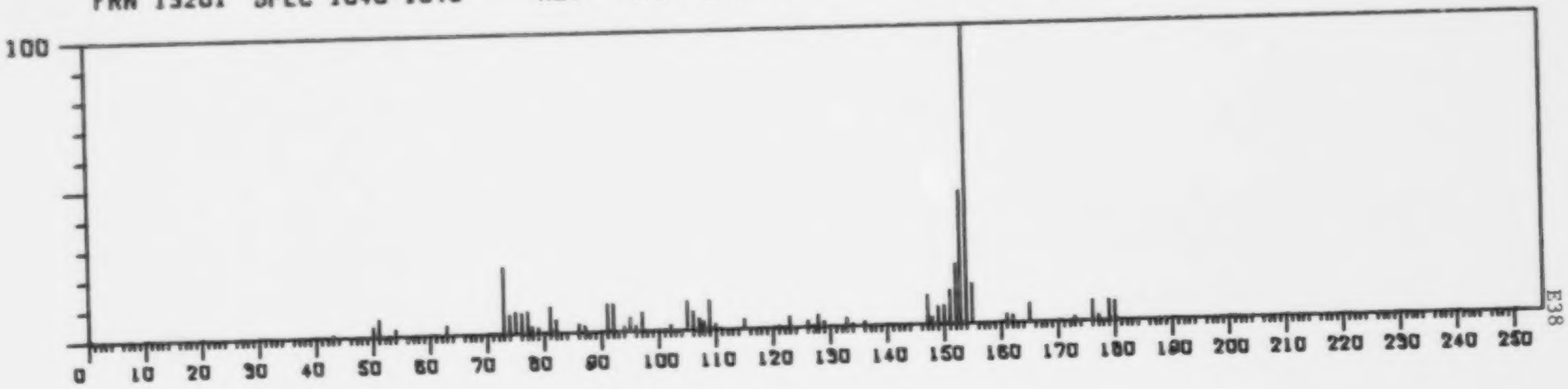
FRN 13201 SPEC 1557 RET. TIME 55. 3 N-TRIDECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1648-1640 RET. TIME 58. 3 BIPHENYL



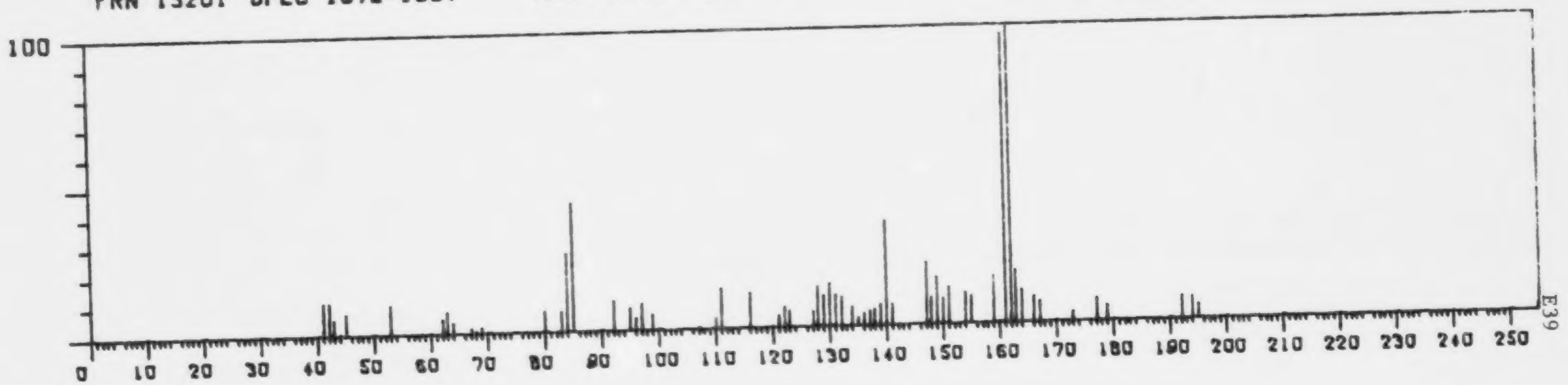
E38

AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 1672-1667 RET. TIME 59. 1 DIMETHYL BENZOTHIOPHENE

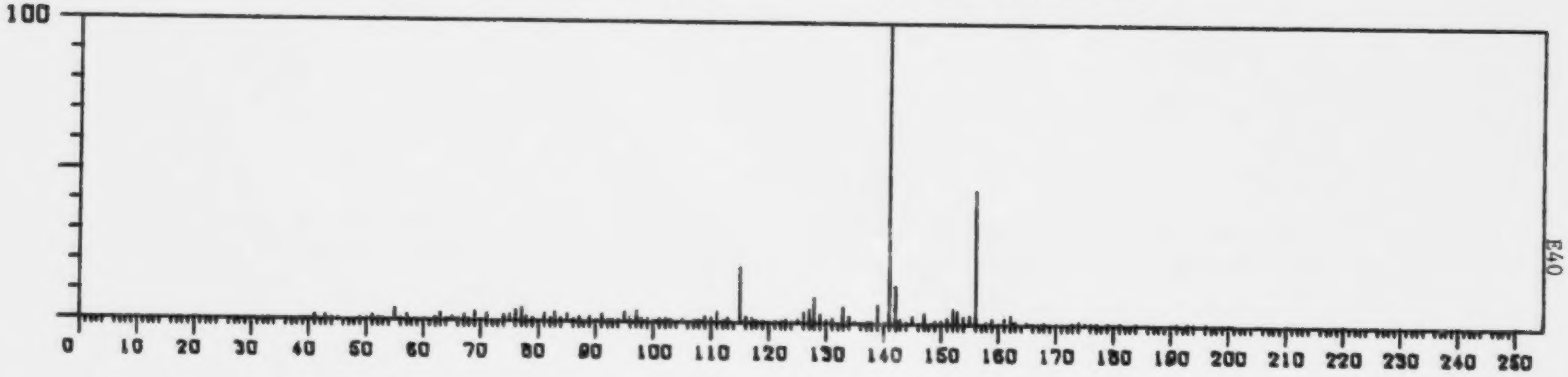


AVGD SPECT

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

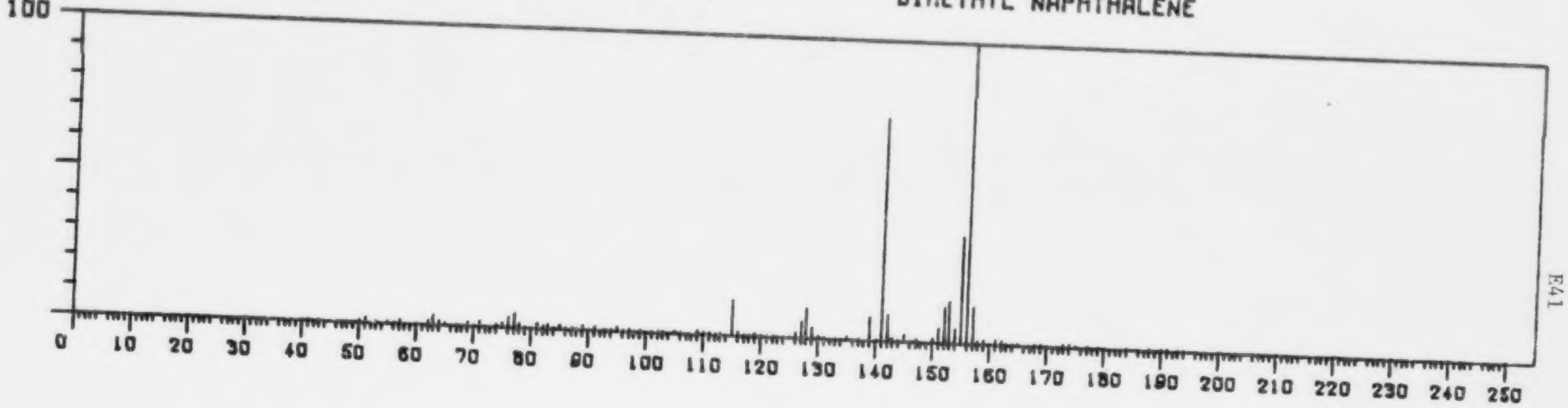
FRN 13201   SPEC 1687   RET. TIME 58. 5   ETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

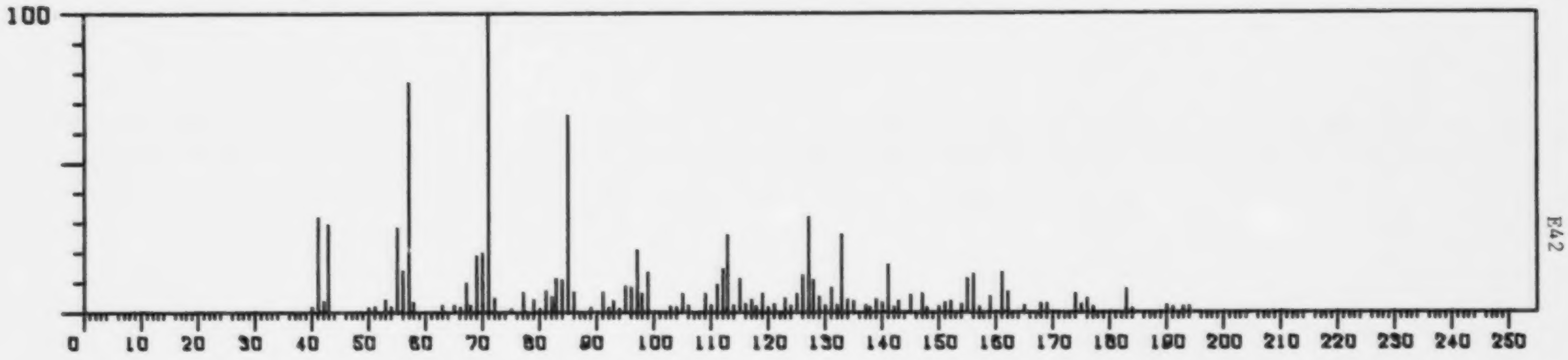
FRN 13201 SPEC 1714 RET. TIME 60. 4 DIMETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

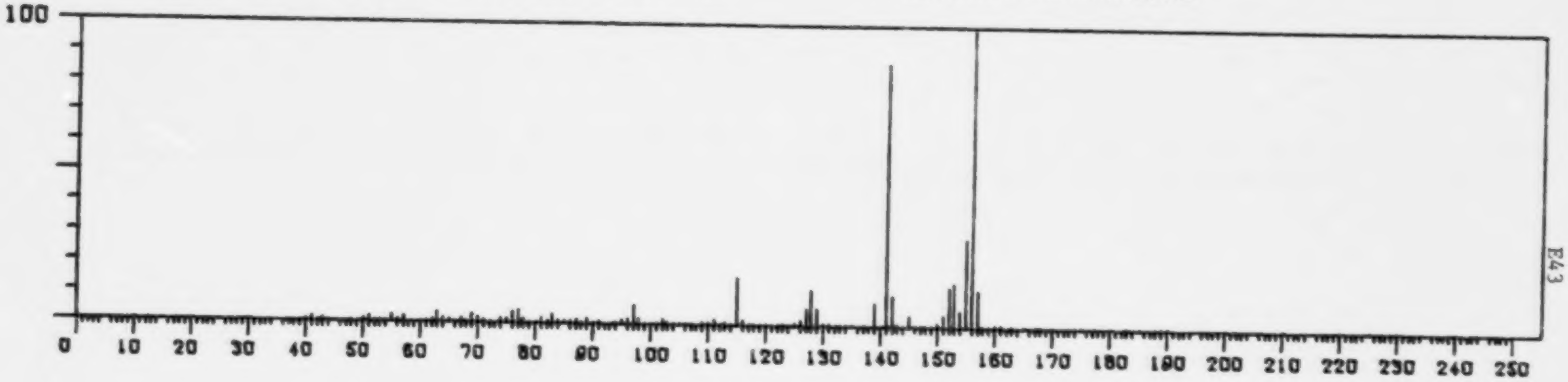
FRN 13201 SPEC 1724   RET. TIME 60. 7   C13 ALKANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

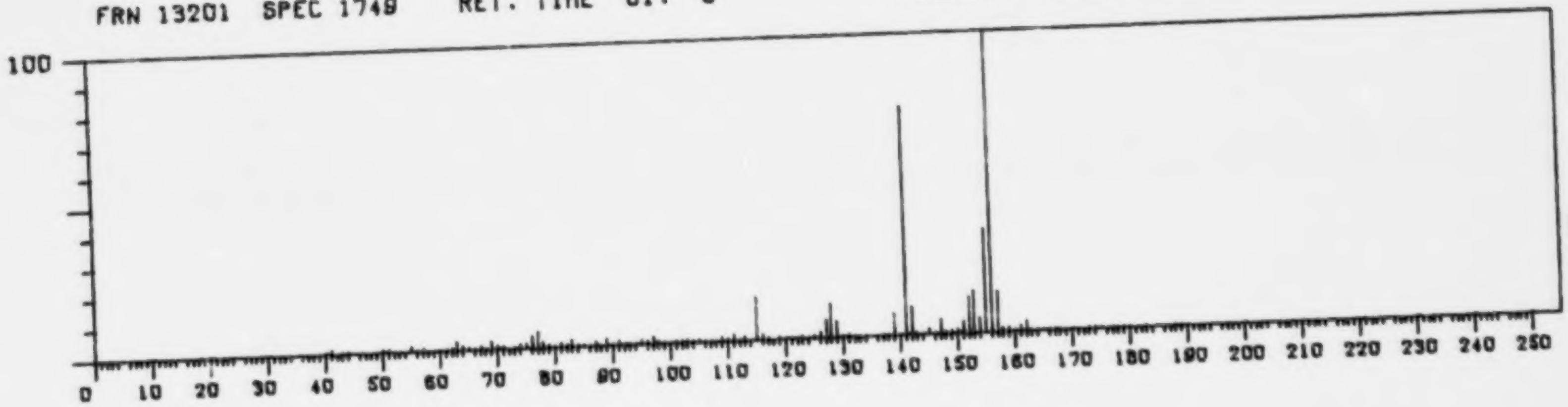
FRN 13201 SPEC 1743 RET. TIME 61. 3 DIMETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1749 RET. TIME 61. S DIMETHYL NAPHTHALENE

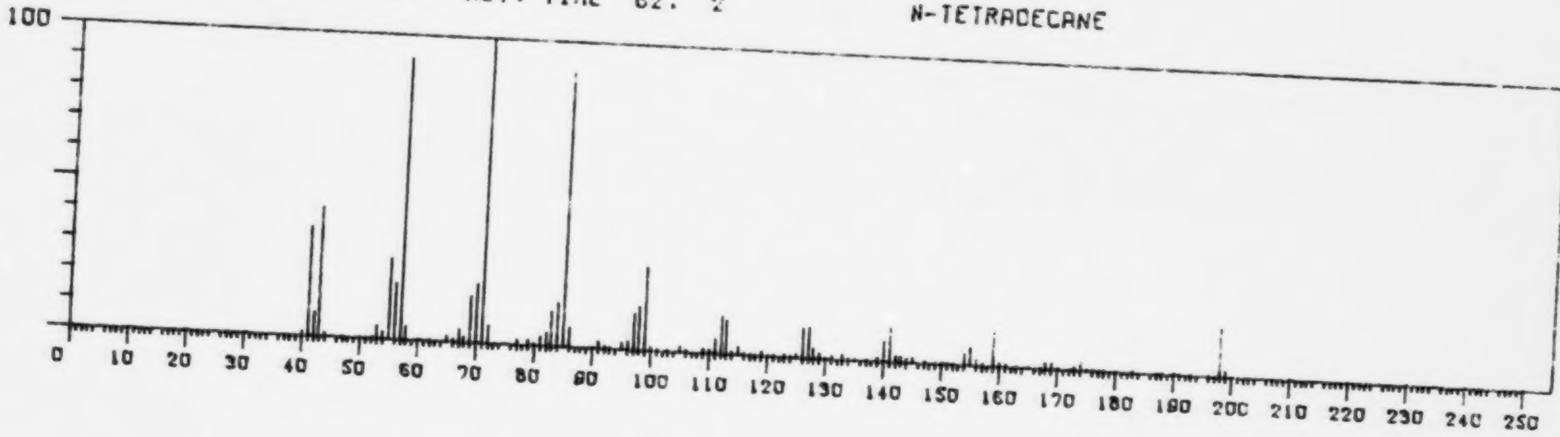


E44

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 1772 RET. TIME 62. 2 N-TETRADECANE

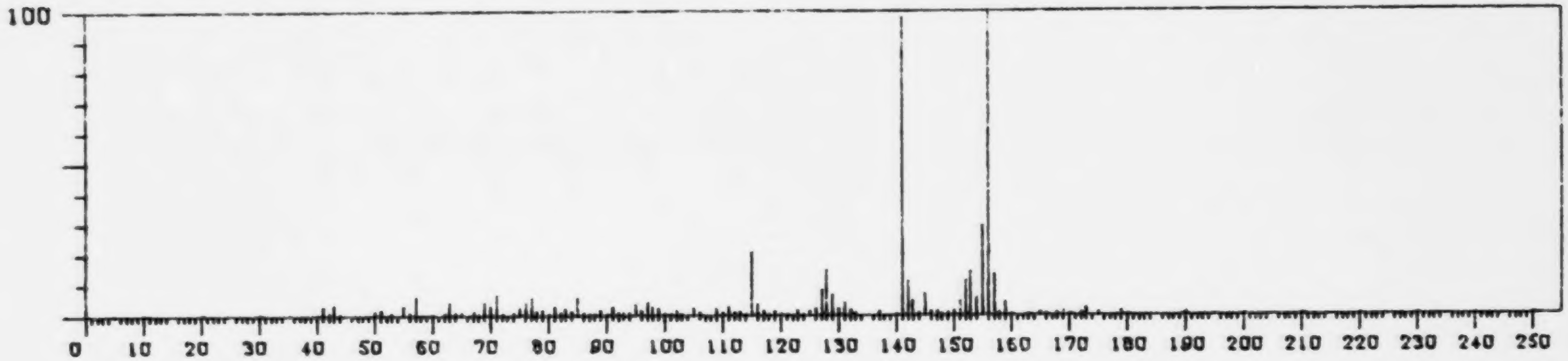


E45

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

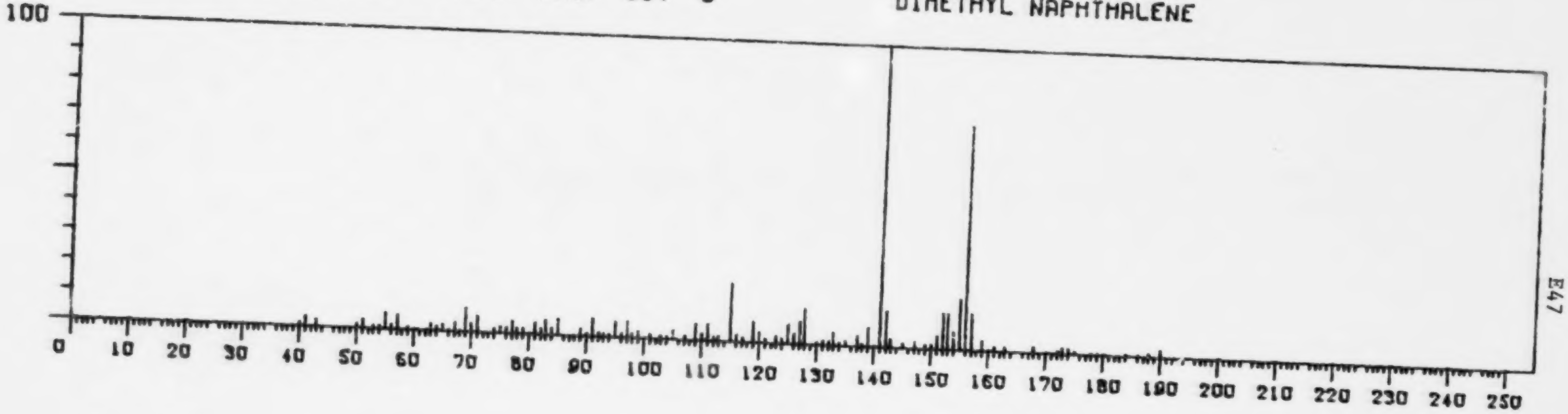
FRN 13201 SPEC 1782 RET. TIME 62. 5 DIMETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

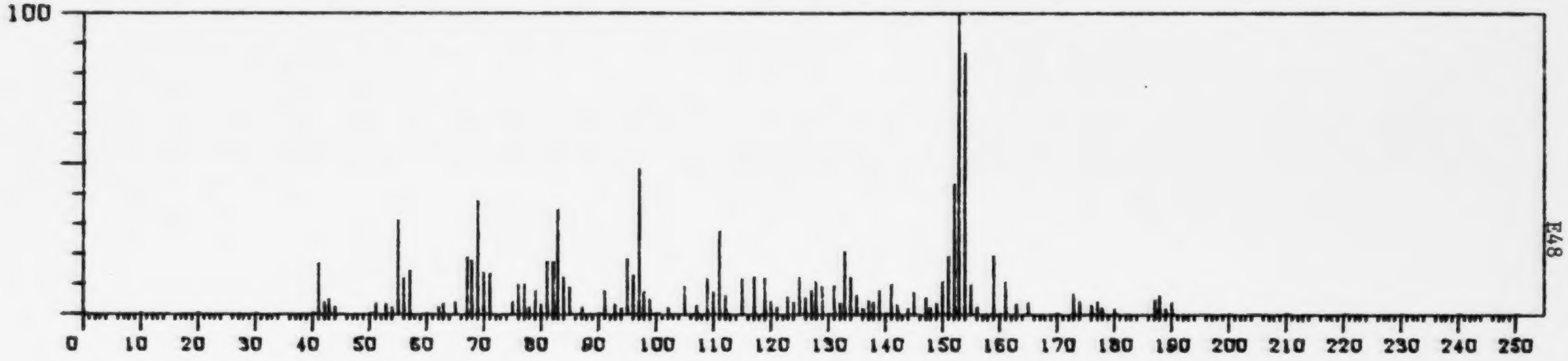
FRN 13201 SPEC 1808 RET. TIME 63. 3 DIMETHYL NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

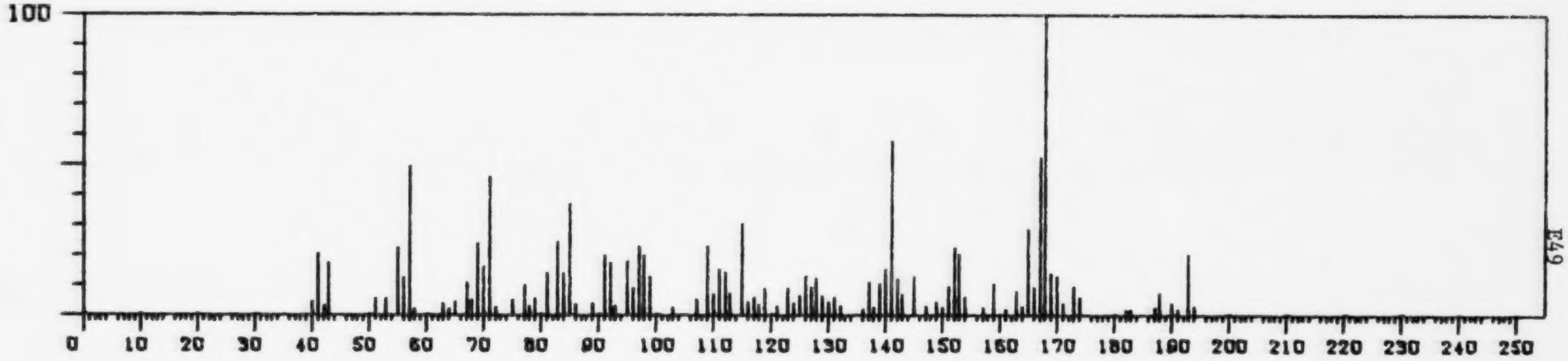
FRN 13201 SPEC 1858 RET. TIME 64. 9 ACENAPHTHENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

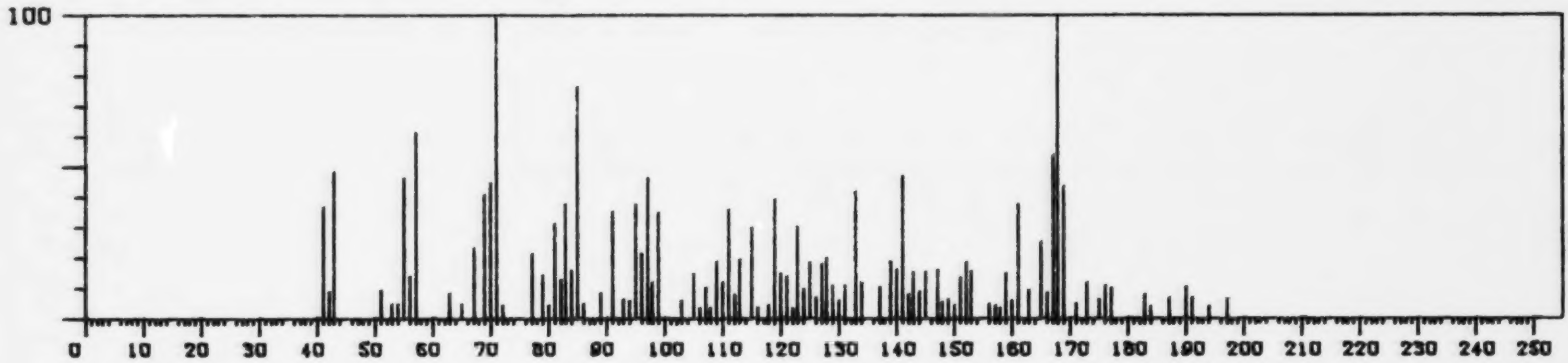
FRN 13201 SPEC 1872 RET. TIME 65. 4 METHYL BIPHENYL



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

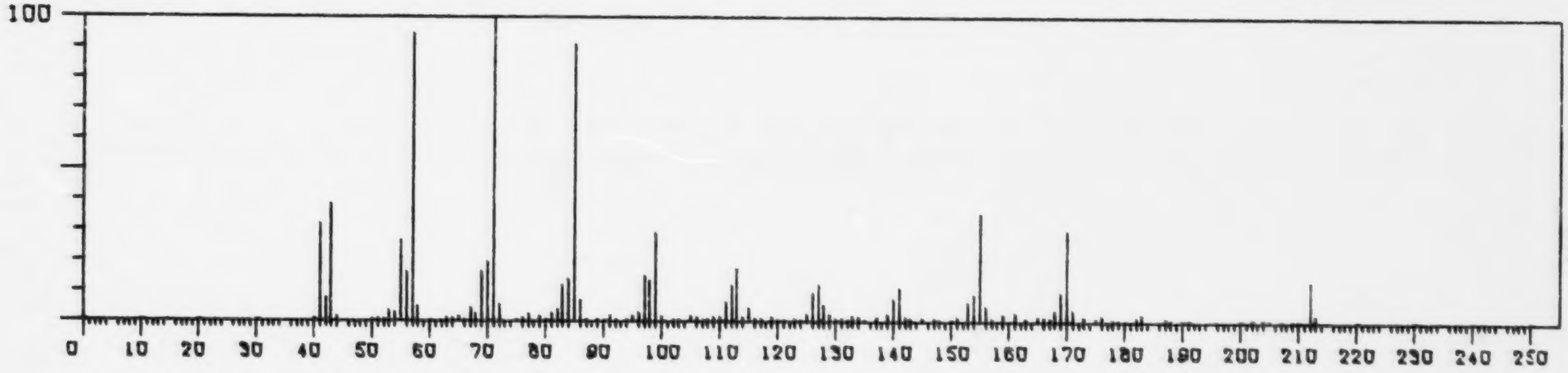
FRN 13201   SPEC 1891   RET. TIME   66.   0   METHYL BIPHENYL



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

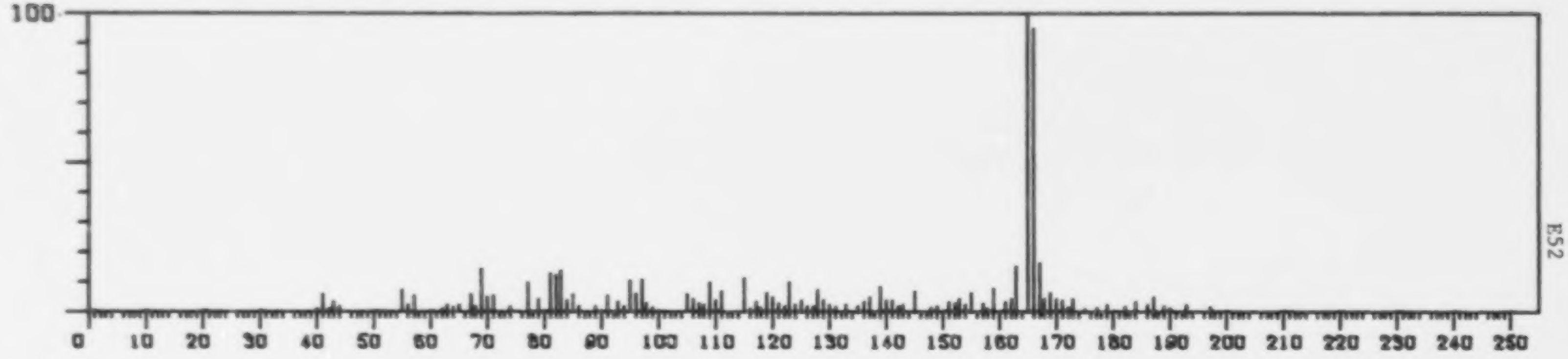
FRN 13201 SPEC 1973 RET. TIME 68. 6 N-PENTADECANE & SOME C3-NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2052 RET. TIME 71. 1 FLUORENE

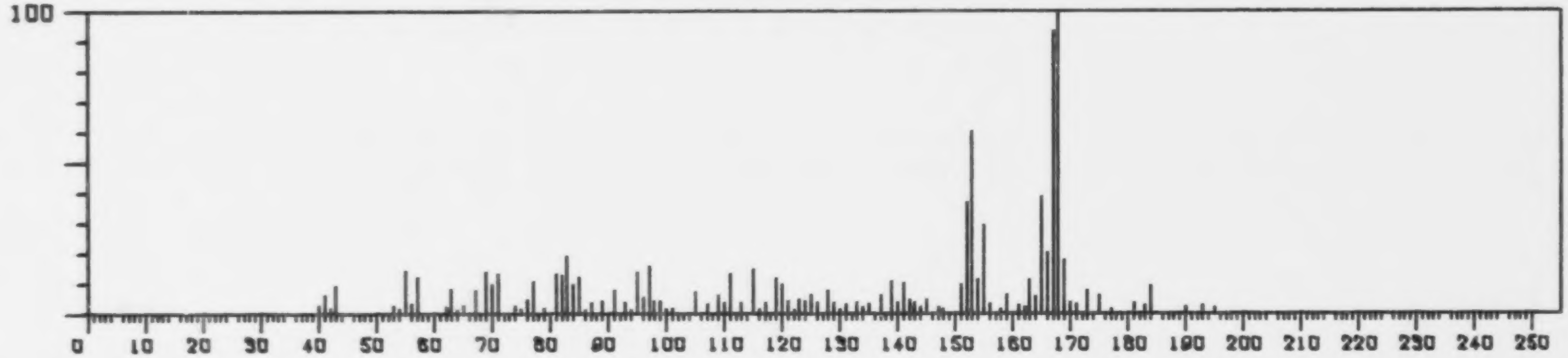


E52

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

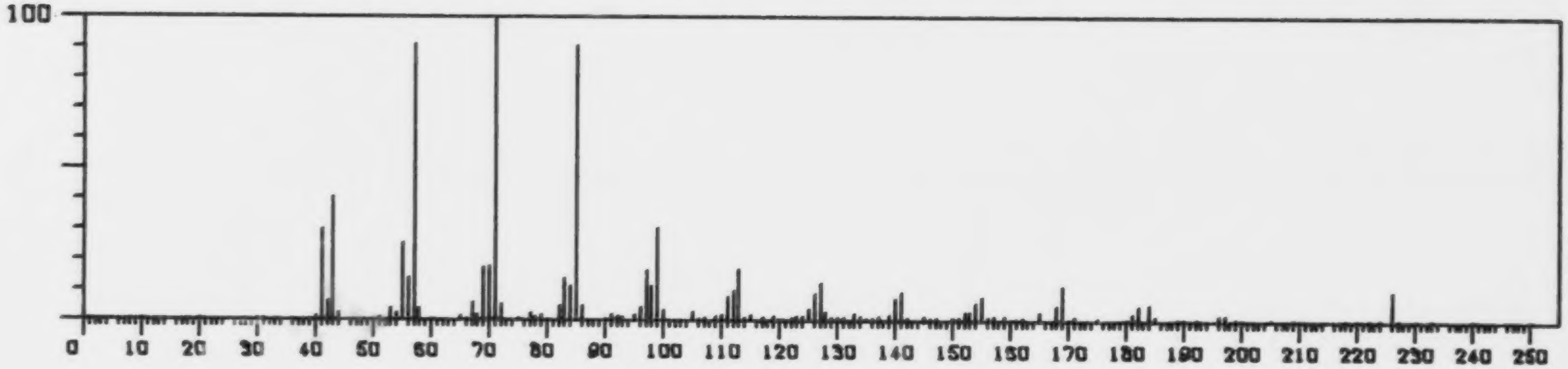
FRN 13201   SPEC 2088   RET. TIME 72. 3   METHYL ACENAPHTHENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

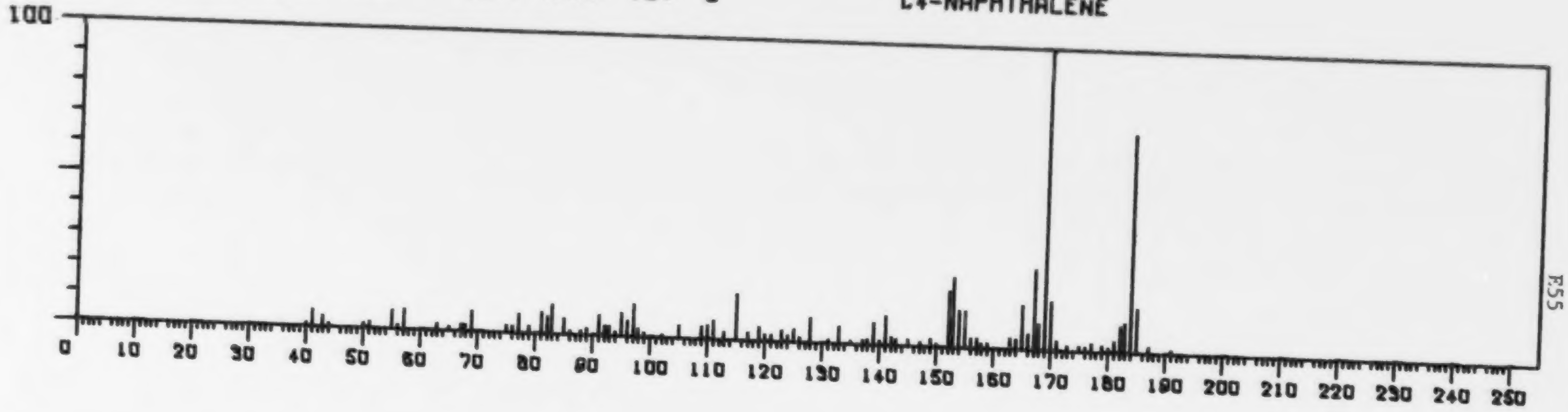
FRN 13201 SPEC 2167 RET. TIME 74. B HEXADECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2188 RET. TIME 75. 8 C4-NAPHTHALENE

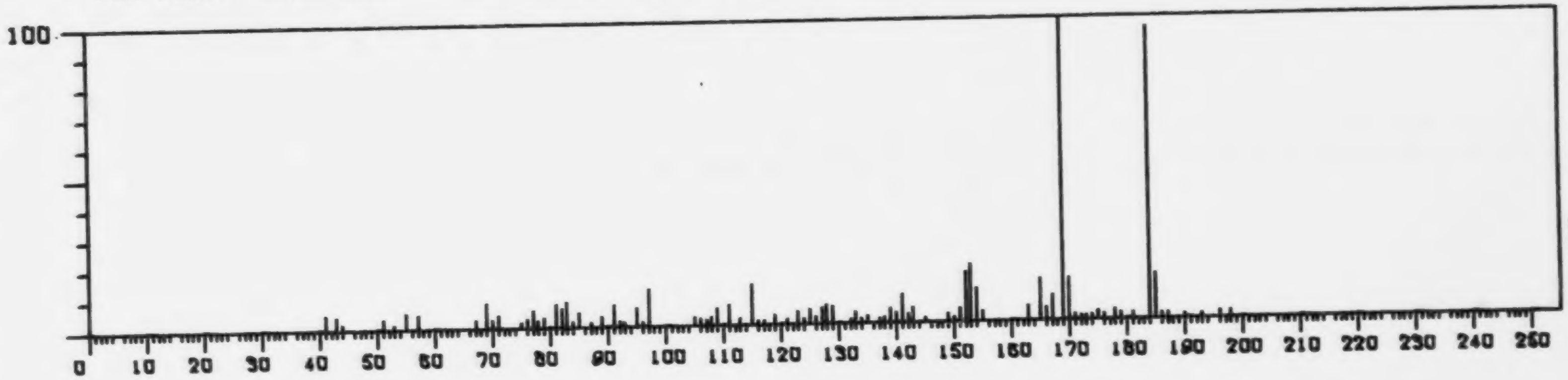


E55

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1,20,3 U

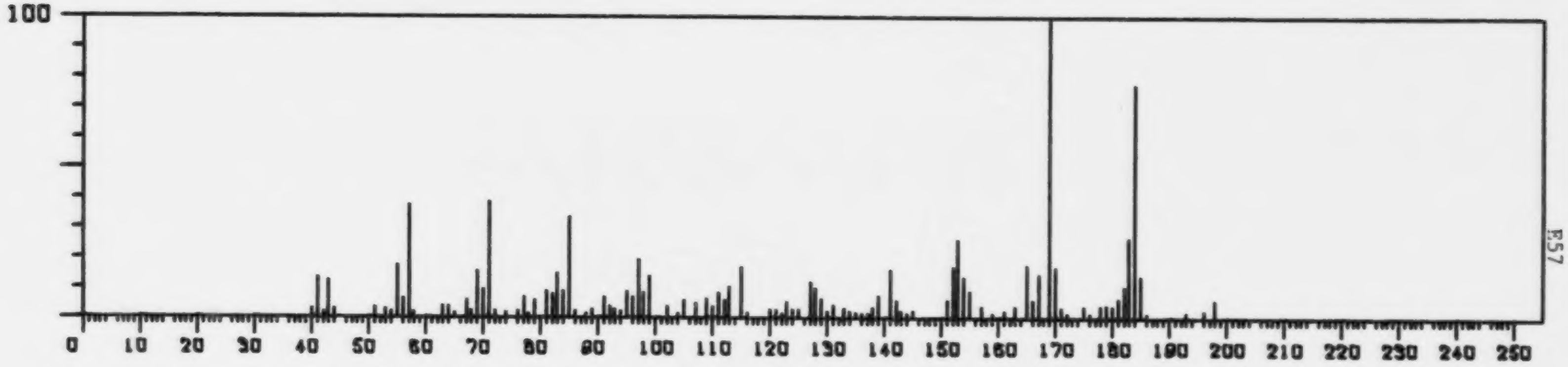
FRN 13201 SPEC 2235   RET. TIME 77. 0   C4-NAPHTHALENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2261 RET. TIME 77. 8 C4-NAPHTHALENE

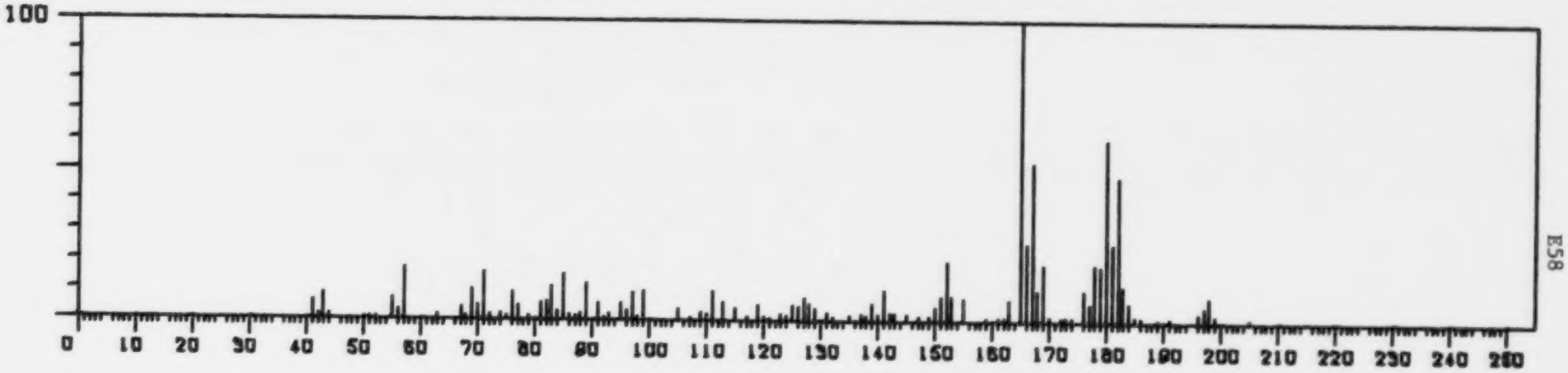


E57

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

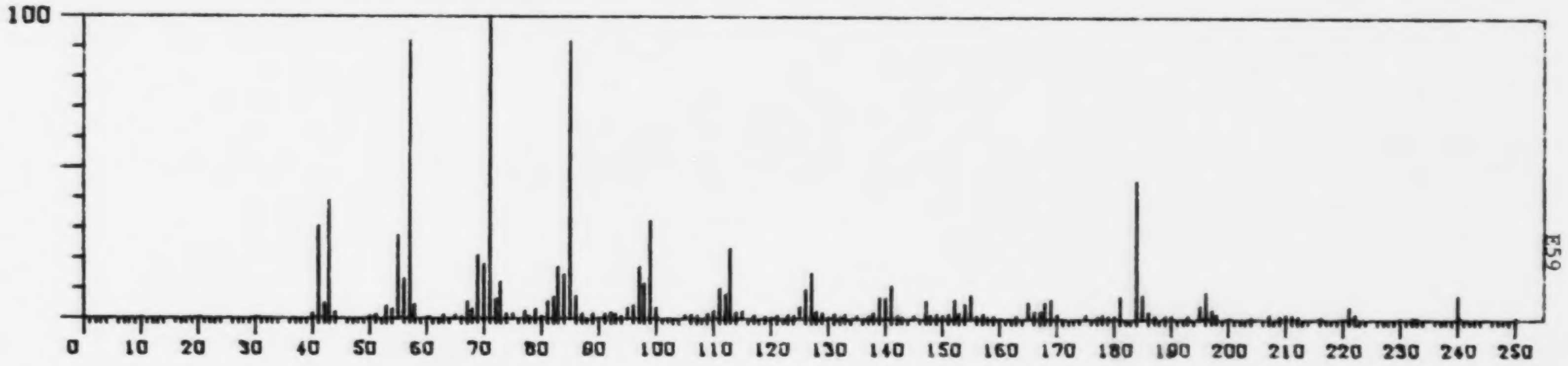
FRN 13201 SPEC 2278 RET. TIME 78. 3 METHYL FLUORENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

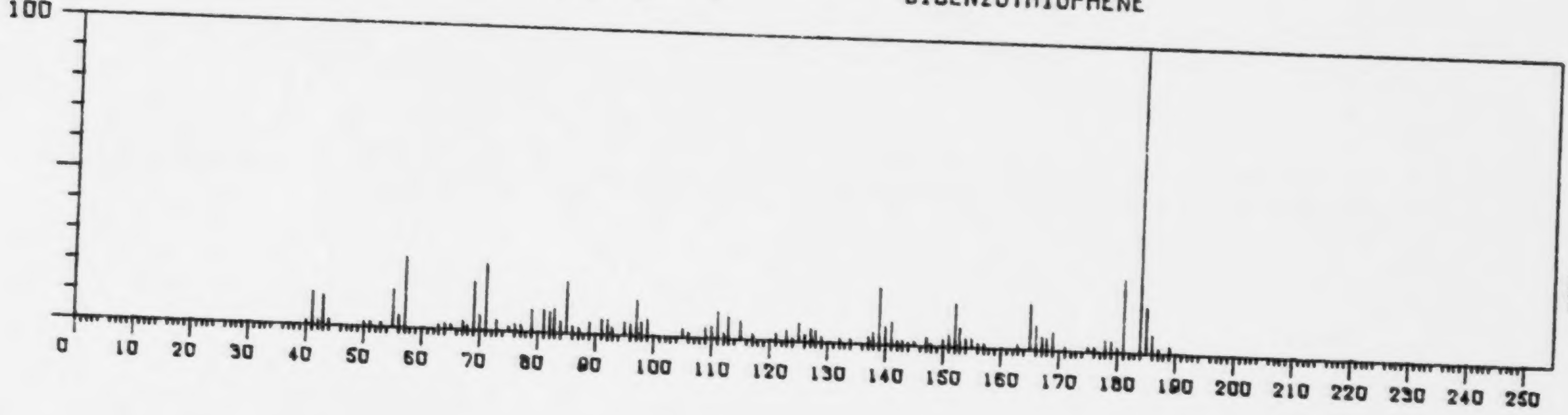
FRN 13201   SPEC 2347   RET. TIME 80. 5   N-HEPTADECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

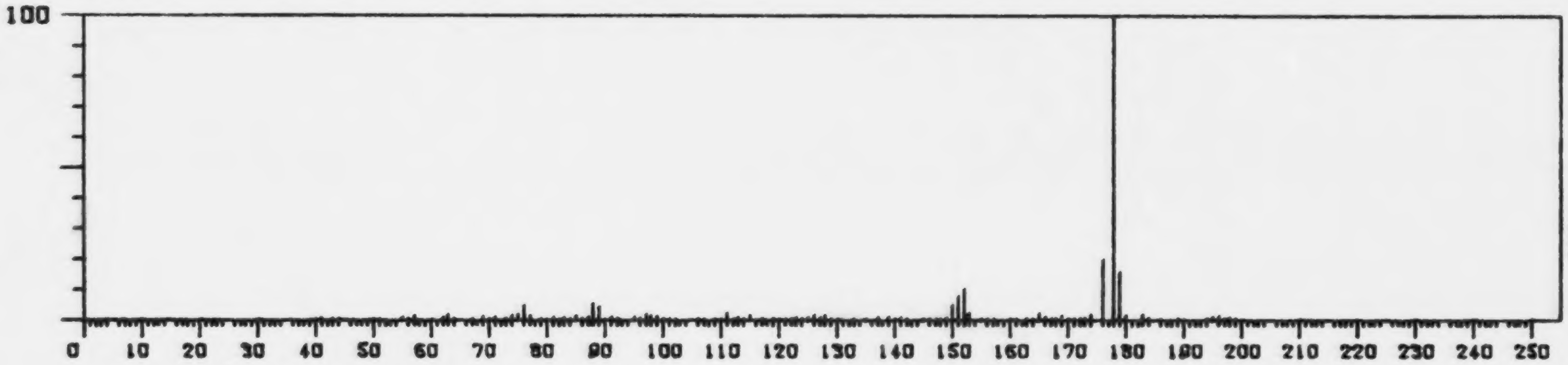
FRN 13201 SPEC 2350 RET. TIME 80. 6 DIBENZOTHIOPHENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

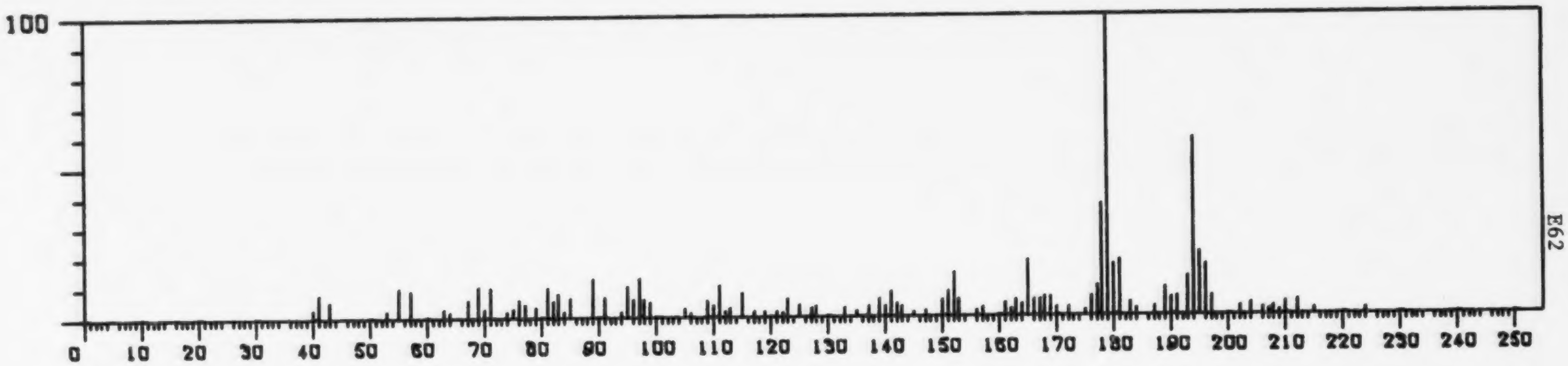
FRN 13201   SPEC 2399   RET. TIME 82. 2   ANTHRACENE/PHENANTHRENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2476 RET. TIME 84. 6 C2-FLUORENE

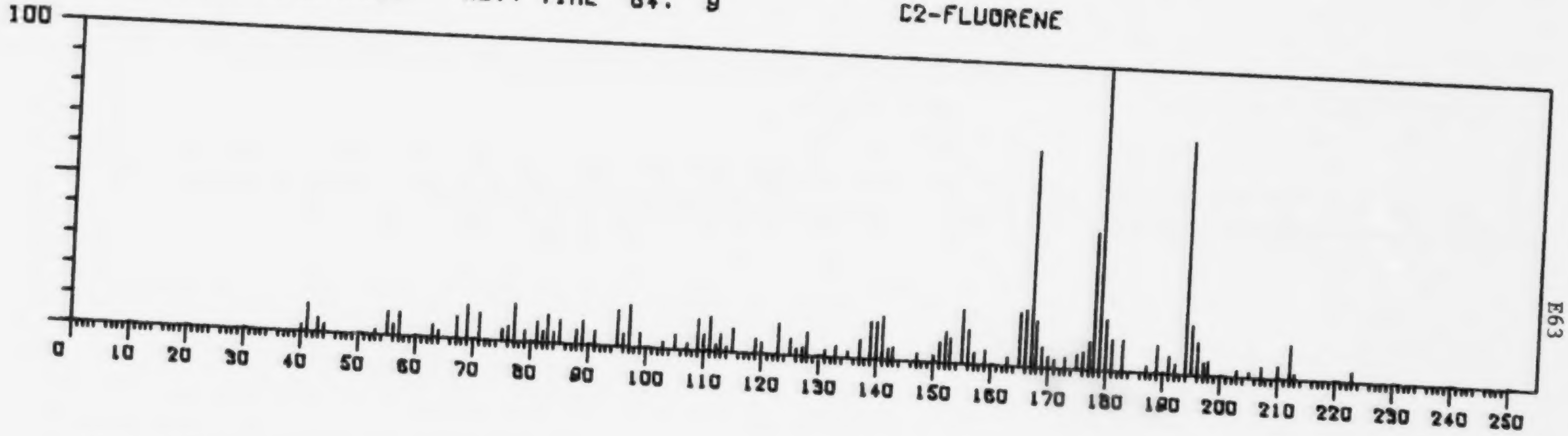


E62

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

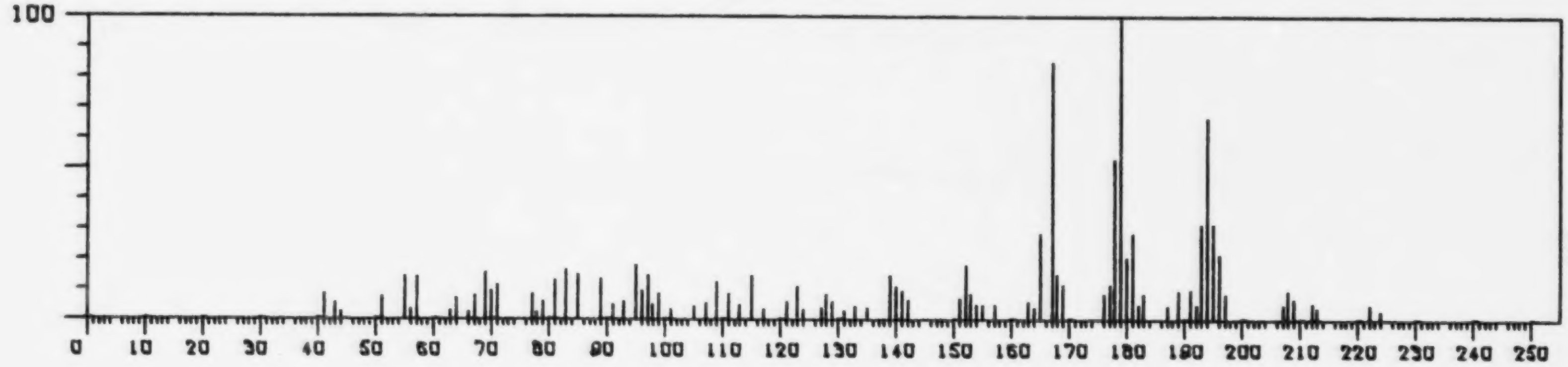
FRN 13201 SPEC 2487 RET. TIME 84. 9 C2-FLUORENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

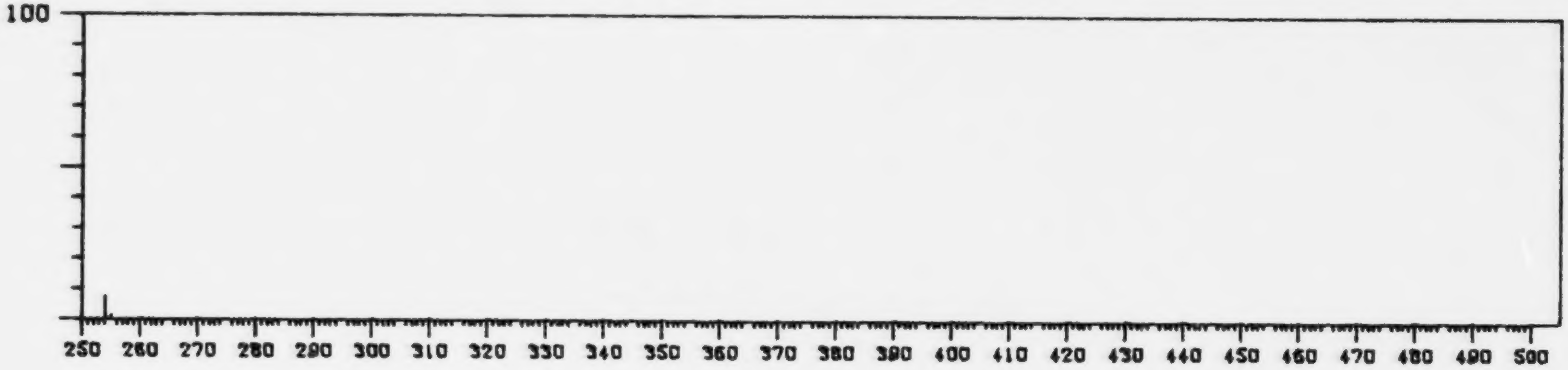
FRN 13201 SPEC 2497 RET. TIME BS. 2 C2-FLUORENE



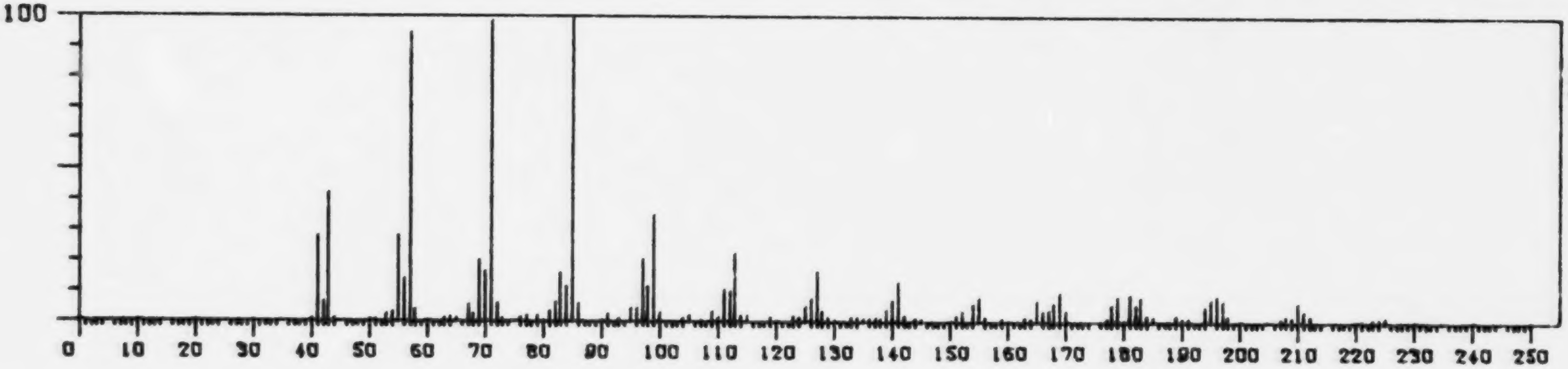
DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201   SPEC 2521   RET. TIME 86. 0   N-OCTADECANE



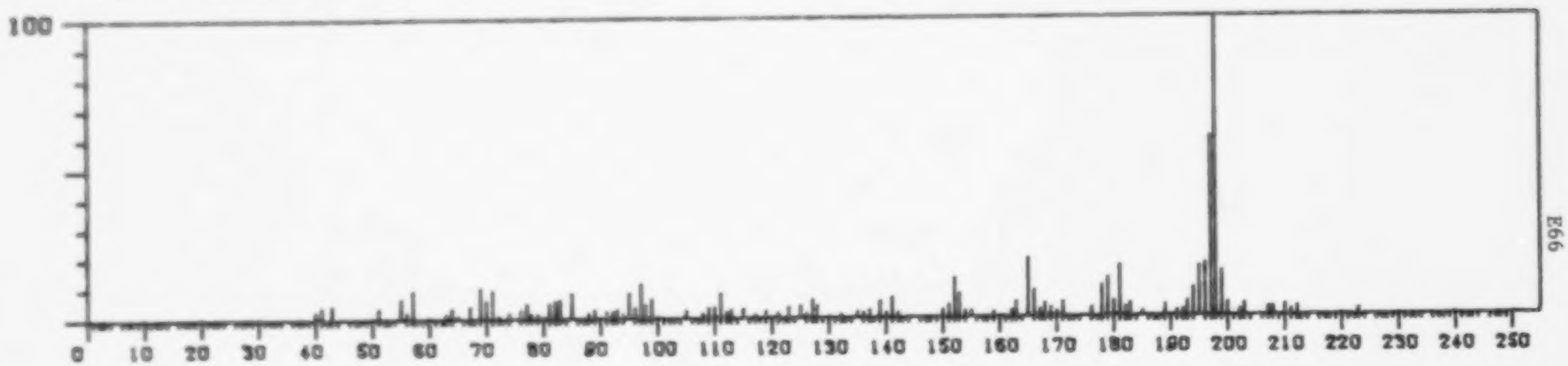
FRN 13201   SPEC 2521   RET. TIME 86. 0   N-OCTADECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

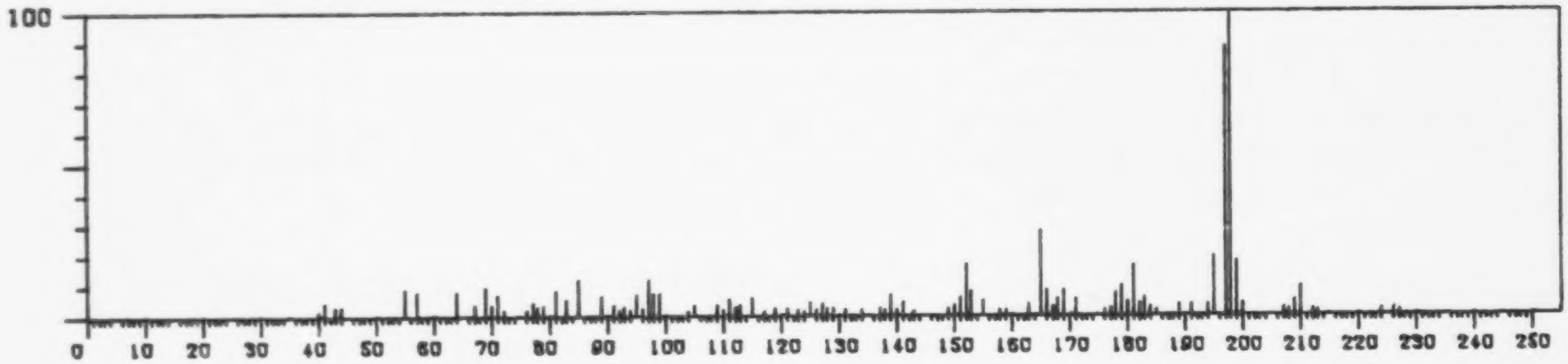
FRN 13201   SPEC 2528   RET. TIME 86. 2   METHYL DIBENZOTHIOPHENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

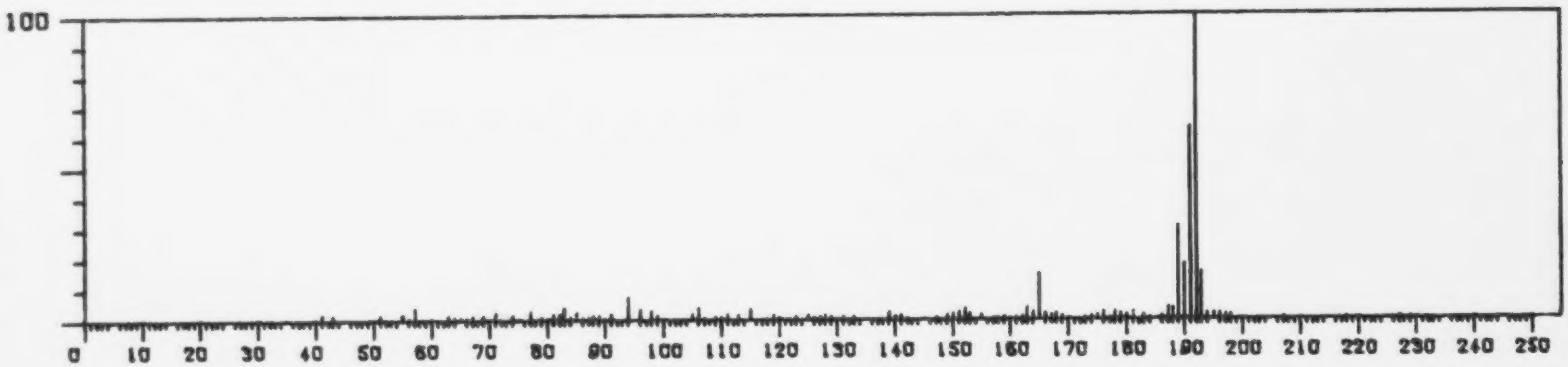
FRN 13201 SPEC 2558 RET. TIME 87. 3 METHYL DIBENZOTHIOPHENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

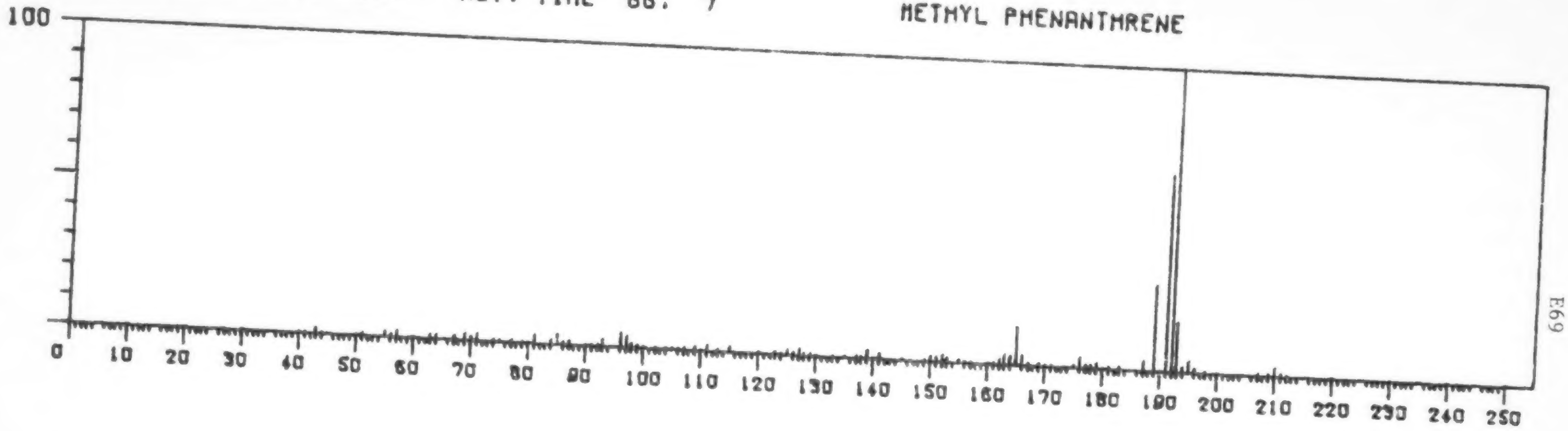
FRN 13201 SPEC 2597 RET. TIME BB. 5 METHYL PHENANTHRENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

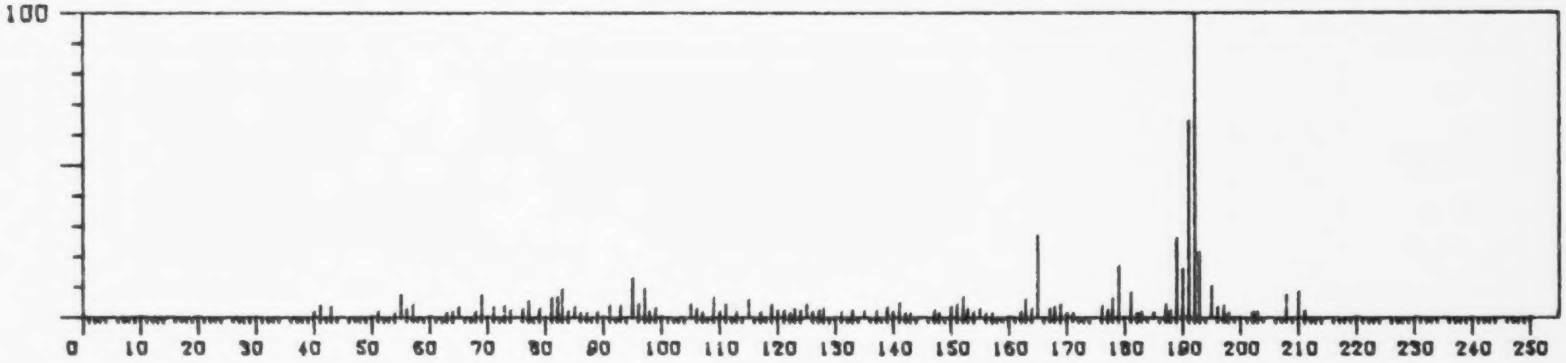
FRN 13201 SPEC 2605 RET. TIME 88. 7 METHYL PHENANTHRENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1,20,3 U

FRN 13201   SPEC 2631   RET. TIME 89. 6   2-METHYL ANTHRACENE

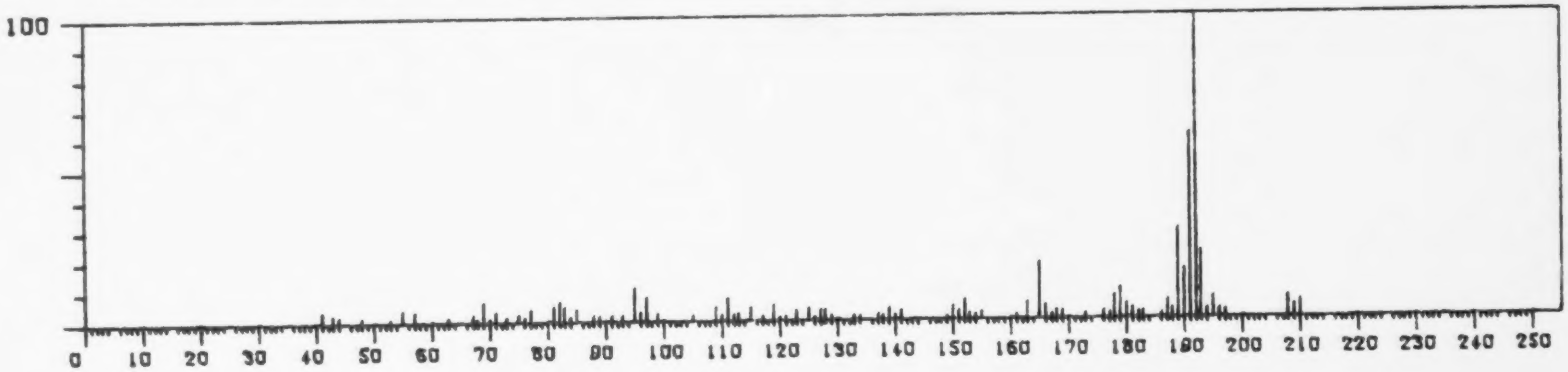


E70

DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

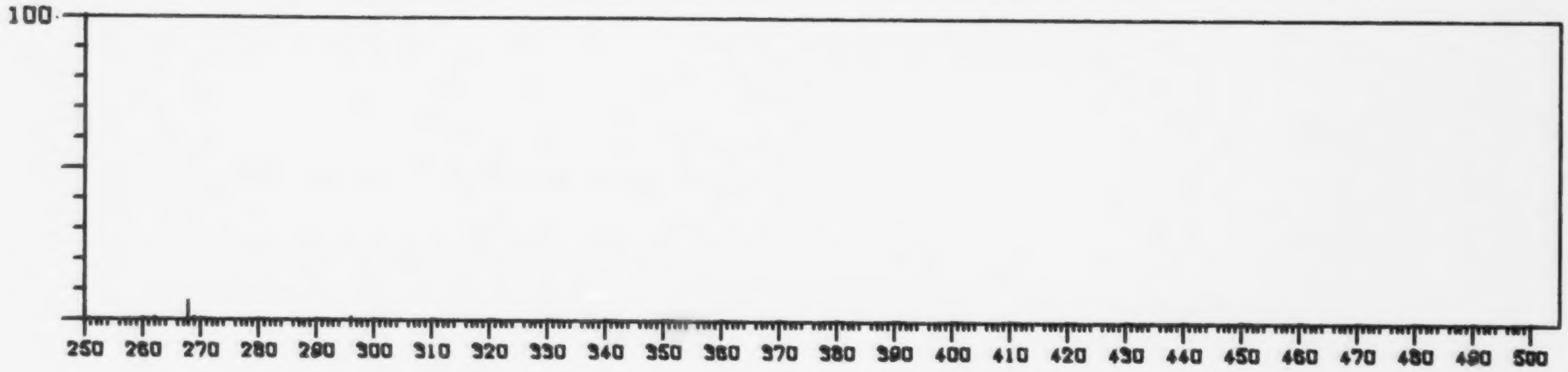
FRN 13201 SPEC 2641 RET. TIME 89. 9 1-METHYL ANTHRACENE



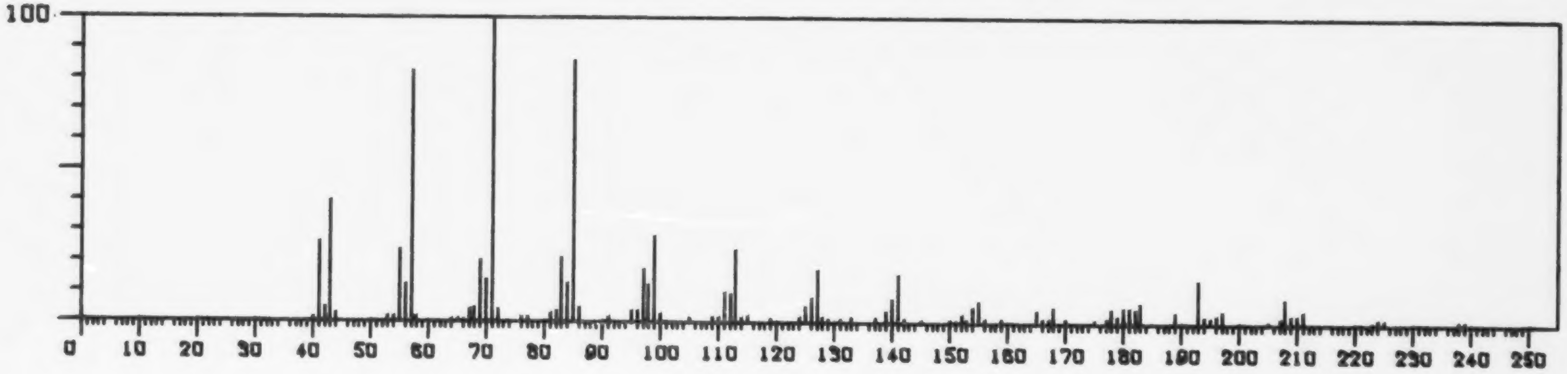
DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 2684 RET. TIME 81. 2 N-NONADECANE



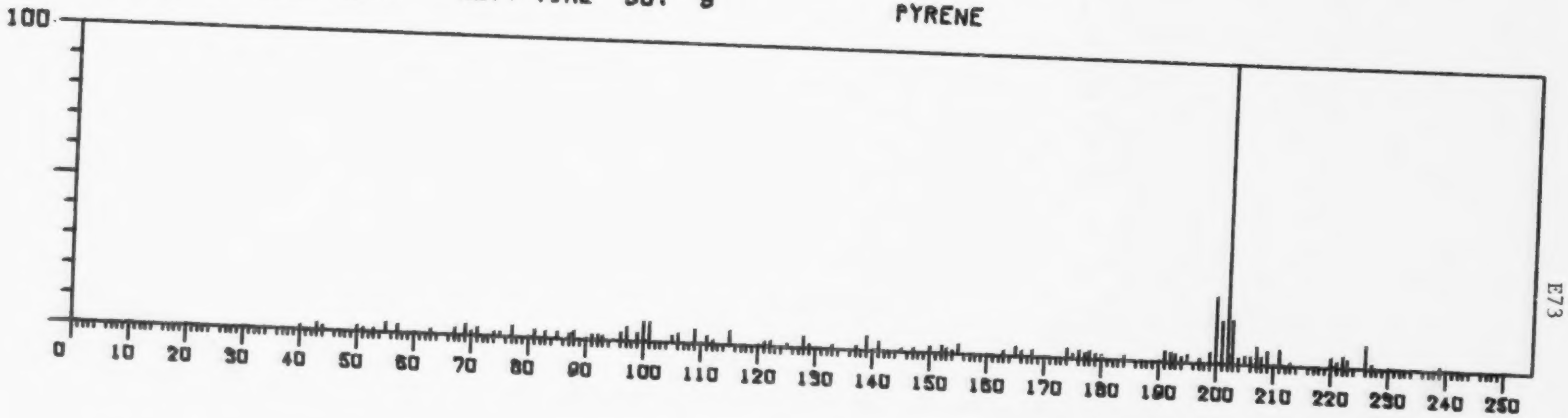
FRN 13201 SPEC 2684 RET. TIME 81. 2 N-NONADECANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

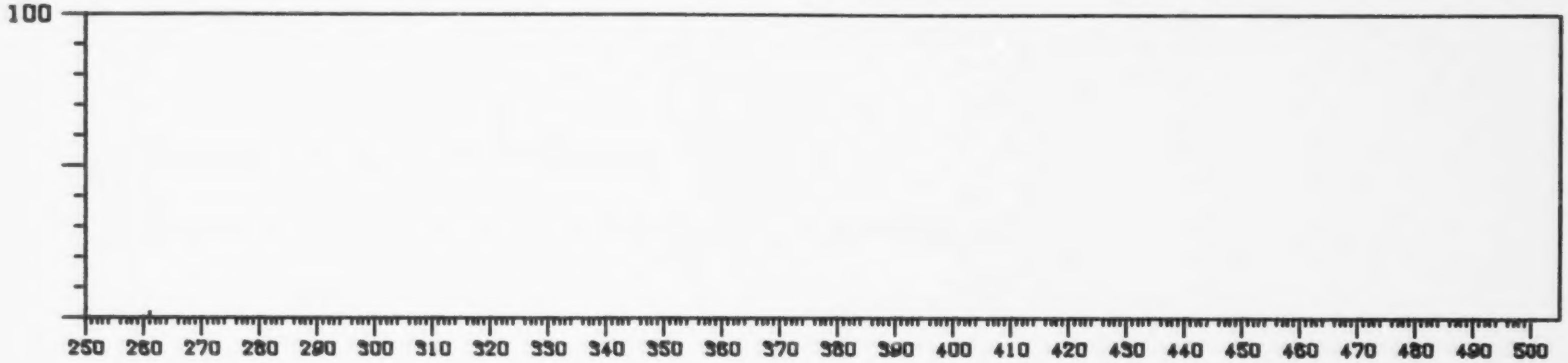
FRN 13201 SPEC 2923 RET. TIME 98. 9 PYRENE



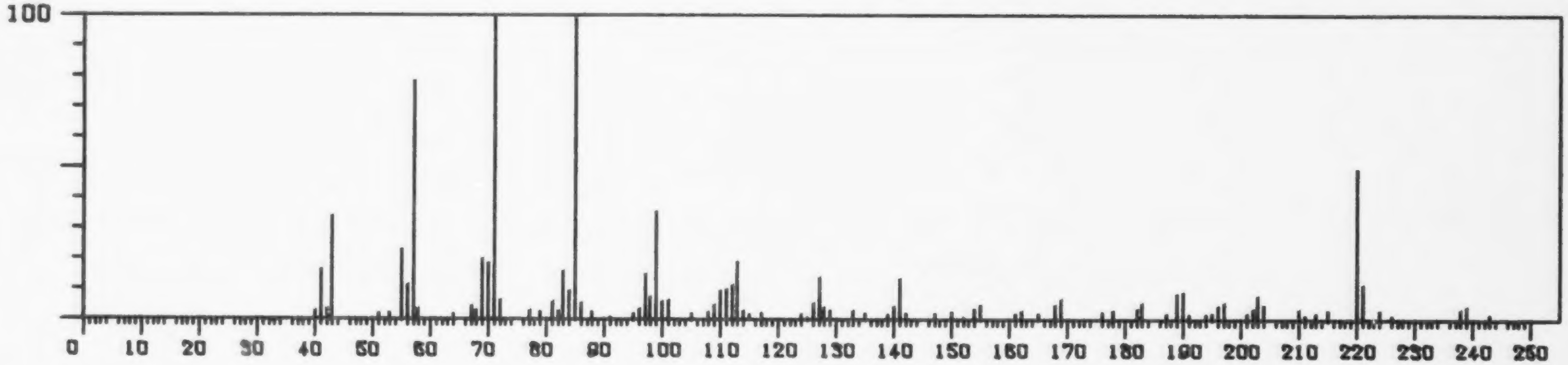
DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC -2980+2993+2993-3001 RET. TIME 101. 1 N-HENEICOSANE



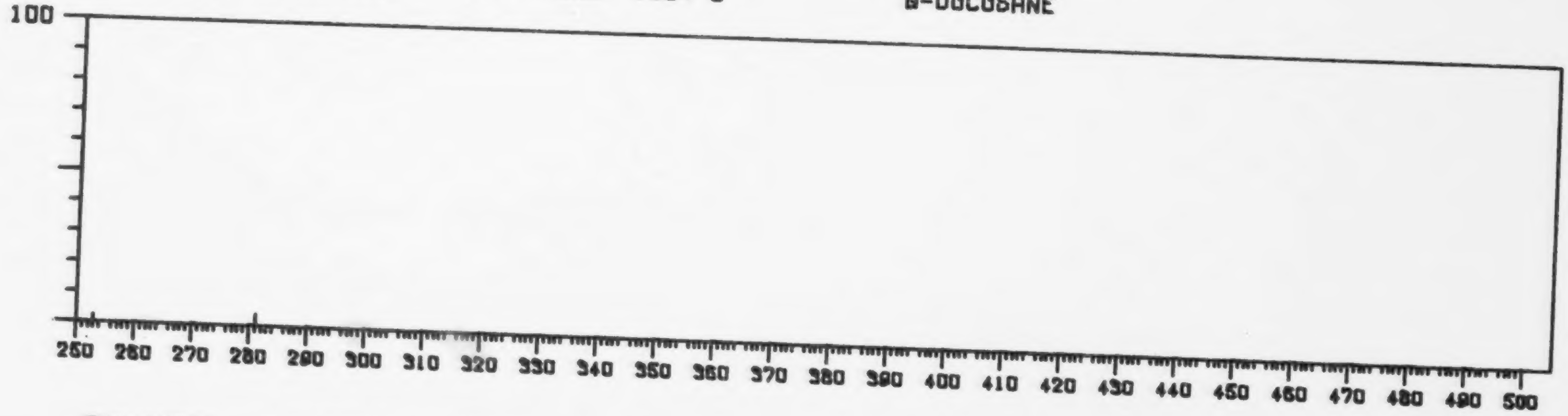
FRN 13201 SPEC -2980+2993+2993-3001 RET. TIME 101. 1 N-HENEICOSANE



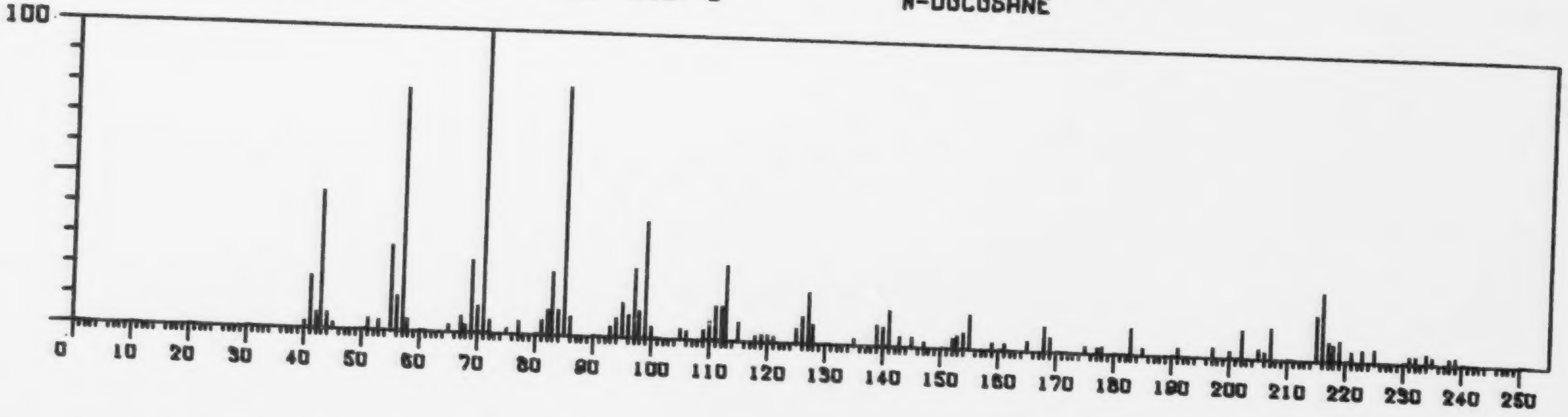
DAF-1234-A-NEUTRAL/F-ME/CH2CL2.OIL 100-FOLD.REF DRG

SOM OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 UL

FRN 13201 SPEC 3138 RET. TIME 105. 6 N-DOCOSANE



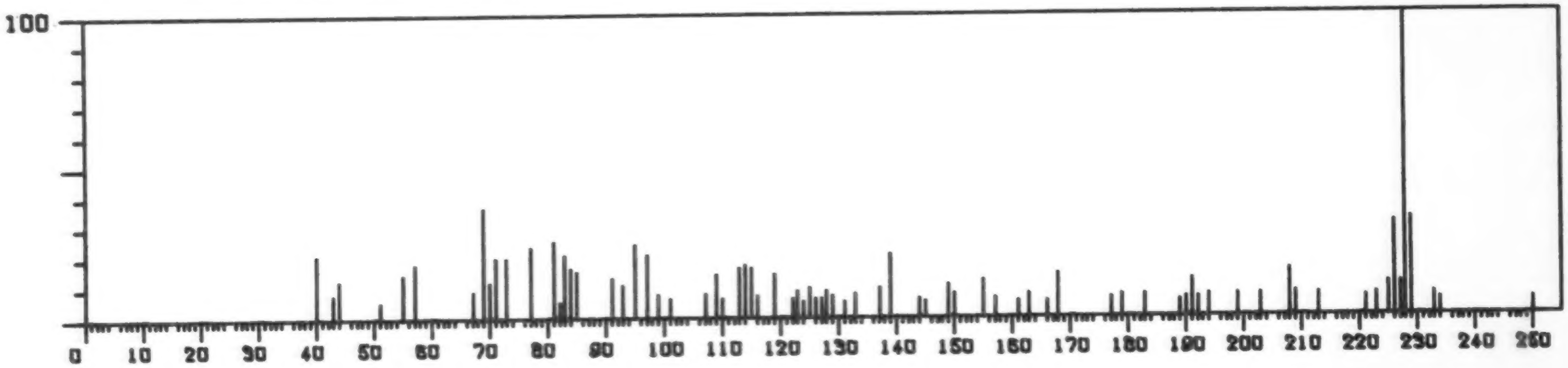
FRN 13201 SPEC 3138 RET. TIME 105. 6 N-DOCOSANE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2,DIL 100-FOLD,REF ORG

50M OV-101,LP AT 2 DEG/MIN,TEMP 1,20,3 U

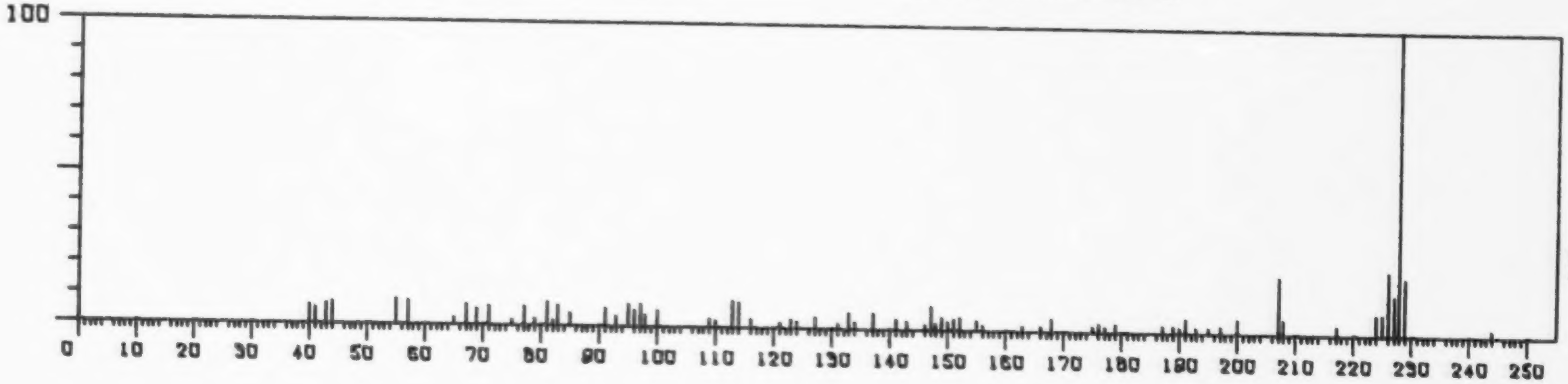
FRN 13201 SPEC 3388 RET. TIME 113. 8 CHRYSENE



DAF-1234-A-NEUTRAL/F-ME/CH2CL2.DIL 100-FOLD.REF ORG

50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

FRN 13201 SPEC 3407 RET. TIME 114. 2 1.2-BENZANTHRACENE



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50M OV-101.LP AT 2 DEG/MIN.TEMP 1.20.3 U

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